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British Association for the Advancement of Science

Reports on colloid chemistry and its general industrial application.
Vol.1.First report,1917.

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Department of Scientific and Industrial Research.

British Association for the Advancement of Science.

Reports on colloid chemistry

FIRST REPORT

1917

ON

COLLOID CHEMISTRY

AND ITS

GENERAL AND INDUSTRIAL APPLICATIONS.

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PREFATORY NOTE.

During recent years a Committee under the Chemical Section of the British Association for the Advancement of Science have been engaged in preparing for publication a series of Reports on Colloid Chemistry and its general and industrial applications. The First Report was published by the British Association in 1917, but owing to difficulties arising from the war it was arranged, on the recommendation of the Advisory Council, that the Second and Third Reports should be published for the Department of Scientific and Industrial Research by H.M. Stationery Office.

The wide sale of these Reports is evidence of the value attached to them by the scientific world and by the industries interested, and as there is still a continued demand for the First Report, of which the earlier edition is now sold out, it has been decided to reprint it under the arrangements which have proved so successful with the Second and Third Reports.

It must be understood that the preparation of all the Reports in this series has been entirely the work of the Committee of the British Association, who assume full responsibility for all statements of opinion or of fact contained therein.

Department of Scientific and Industrial Research,
16 and 18, Old Queen Street,
Westminster,
London, S.W. 1.

December, 1920.

Wt. 34427/742—2000—2/21 *T.S*

Colloid Chemistry and its Industrial Applications.—First Report of the Committee, consisting of Professor F. G. Donnan (*Chairman*), Professor W. C. McC. Lewis (*Secretary*), Dr. E. F. Armstrong, *and* Mr. A. S. Shorter.

Introduction.

The Committee was formed with the object of compiling information regarding the advances which have been made in capillary and colloid chemistry with special reference to industrial processes. For this purpose it is essential to take a broad view of the term 'colloid.' The Reports which it is proposed to issue will refer to the more important scientific investigations published in recent years as well as to those possessing a more immediate technical bearing. The Committee has been fortunate in obtaining the collaboration of a number of specialists in various branches of the subject who have undertaken the work of compilation. The advantage of this mode of procedure lies in the fact that the necessary selection and presentation of material has been carried out by those particularly qualified to deal with the various sections concerned. To these gentlemen the Committee would express its deep sense of obligation.

As regards the classification and division of the whole, two methods present themselves: first, a classification according to the nature of the property, principle, or phenomenon concerned, based on the recognised divisions of the science of colloid chemistry, *e.g.*, Coagulation, Viscosity, Adsorption, Peptonisation, &c.; secondly, a classification in terms of the various technical processes themselves, each of which involves in general more than one scientific principle, *e.g.*, the process of Tanning, which includes Adsorption, Coagulation, 'Membrane Equilibria,' &c. Both of these modes of classification have been adopted. This naturally involves a certain amount of overlapping, but it is felt that the disadvantage is not serious. It is hoped that this treatment of the subject-matter will not only be comprehensive, but will serve at the same time to illustrate the close connection which exists between scientific principles and technical practice. At the present time many of the operations in technical colloid chemistry are largely empirical, the scientific basis being unknown or only imperfectly understood. One of the objects which the Committee has had in view is to emphasise the existence of this state of affairs. It is clear that the present position demands a vigorous prosecution of scientific research over the entire range of colloid chemistry.

The marked differences of opinion which exist at the present time in regard to various colloid problems are themselves evidence of the relatively undeveloped state of the subject. As an illustration we might instance the phenomenon of Adsorption. On the one hand, we have the capillary view first stated quantitatively by Gibbs, a view which at the present time occupies a very strong position especially as regards liquid surfaces. On the other hand, we find the capillary idea dropped and the concept of valency beginning to take its place as an explanation of the phenomenon,

more particularly in connection with the condensation of gases upon metallic and other solid surfaces (investigations of Langmuir and others). This is merely illustrative, but it is sufficient to emphasise the point referred to.

A further object of the Committee is to render available as far as is practicable the information on applied colloid chemistry which is believed to exist among chemical technologists at the present time, but which from its possibly unco-ordinated nature is not regarded as suitable for publication through the ordinary channels. It is hoped that those possessing such 'incidental' information, as well as those whose information regarding various special technical colloid problems is of a more systematic nature, will see their way to communicate with the Secretary (Muspratt Laboratory, University of Liverpool), so that the Committee may be able to consider the question of publication of such material as it considers suitable. In the present state of the subject it is felt that more will be gained by co-operation of this kind than by isolated investigation; and further it is believed that much may be made public without detriment to individual interests.

It will be obvious that under the present exceptional conditions the subjoined Report is of a preliminary nature only.

As regards classification according to scientific subject, one subject only, namely, the Viscosity of Colloid Systems, is dealt with. As regards classification according to technical processes and applications generally, the following subjects are treated:—

1. Tanning.
2. Dyeing.
3. Fermentation Industries.
4. Rubber.
5. Starch, Gums, Albumin, Gelatine, and Gluten.
6. Cements.
7. Nitrocellulose Explosives.
8. Celluloid.
9. Physiological and Bio-chemical Subjects.

It is proposed to deal with other branches of colloid chemistry in next year's Report.

VISCOSITY OF COLLOIDS.

By EMIL HATSCHEK, *Sir John Cass Technical Institute, London.*

General Review.

An excellent general survey of the subject as it stood at that time is given by the General Discussion by the Faraday Society in 1913. The most important advance since then is the proof, by v. Smoluchowski, that the electric charge on suspensoid particles contributes to the viscosity of systems containing such particles, and the numerical expression deduced by him for this increase.

The Einstein formula, according to which the increase in viscosity is simply proportional to the aggregate volume of suspended spheres, has again been tested by Humphrey and Hatschek on a suspension of starch grains (average diameter 3μ) in a mixture of carbon tetrachloride and toluene. The increase in viscosity was found to be more than linear for concentrations between 2 and 6 per cent.; in addition the viscosity

was found to be a function of the rate of shear, and not, as has been tacitly assumed in measurements with the capillary viscometer, independent of it. A similar result for emulsoid sols had been obtained by Hatschek in 1913. The theoretical reasons why Einstein's formula fails, and the general difficulties of a universally applicable formula for systems of two liquid phases, have been fully discussed by v. Smoluchowski.

As regards emulsoid sols, Hatschek's formula has been applied to the calculation of the solvation factors of proteins by Miss Chick and of rubber in various solvents by Kirchof. The latter's results are of interest, as a comparison is possible between the amounts thus calculated from viscosity measurements and the amounts taken up by the rubber in the preliminary swelling—remarkable agreement exists between the two sets of values. Arrhenius has criticised the figures for proteins, or rather the viscosity formula leading to them, as the hydration factors are much in excess of those found for hydrates of salts in solution. By applying his logarithmic formula to Miss Chick's measurements he obtains hydration factors of the same order as those of electrolytes. Hatschek has, however, shown that the application of Arrhenius's formula to sols in organic solvents (rubber and nitrocellulose) leads to factors which sometimes are negative, and thus without any physical meaning, and sometimes positive, but many times larger than those to which Arrhenius takes exception.

The great importance of viscosity measurements as the most delicate means of tracing slight changes in colloidal solutions is fully recognised, but in the present state of theory all that can be deduced from such measurements is that some change has taken place, the nature of which is either a matter for speculation or for empirical interpretation. As the latter is sufficient in many instances, viscometric methods appear to find increasing use in fields as widely different as the industries of rubber and nitrocellulose on one hand, and physiology and pathology on the other. There is also a fairly general and gratifying tendency towards the use of correctly designed capillary viscometers, instead of the grossly incorrect types used for other industrial purposes.

Further decided progress must depend on the development of theory, which, considering the great inherent difficulties of mathematical treatment and the incompleteness of our knowledge of even simple liquids and binary mixtures, cannot be expected to be rapid, and also on the much extended use of methods of measurements permitting variation of the rate of shear within wider limits than have so far been attained.

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COLLOID CHEMISTRY OF TANNING.

By Professor H. R. PROCTER, *University of Leeds.*

*General Review.**

The conversion of skin into leather is an art dating back many thousand years, and the group of phenomena now classed as capillary or colloid has also been long known, though the relation of the two is a matter of modern knowledge. Under these circumstances it is difficult to know where to begin the discussion, and the question is further complicated by the work of the present writer and his pupils, who have recently shown that much which has been attributed to the surface-action which is implied in the name 'capillary chemistry' is really subject to more general laws, and can be fully explained by mass action, electro-chemical attraction, and osmotic pressure. The title must therefore be taken, with a wider meaning than its etymology would imply, to include much of physical chemistry, complicated, however, by structure and the special properties of colloids.

The skin is constituted of collagen (probably a polymerised anhydride

* Among the abbreviations employed in this Section are the following:—*Coll.* = *Collegium*; *J.A.L.C.A.* = *Journ. of the American Leather Chemists' Association*; *L. Coll.* = *London Collegium*, Jan. 1915 to June 1917; *T.C.S.* = *Transactions of Chemical Society* (*London*).

of gelatine) and physically is a network of fibres of colloidal jelly. In its natural state it has an outer coat of epidermis, with its hair and sebaceous and sudoriferous glands, but it is not necessary in this Report to consider in detail the chemical, mechanical, and bacteriological processes which are used to free it from these appendages or to separate its fibre-bundles into their smaller constituent fibres. These gelatinous fibres in the dried raw hide adhere together to form an almost homogeneous horny mass, and the problem of the tanner is so to treat them, either by chemical change or by surface-coating, as to prevent their adhesion, so that on drying they remain isolated and free to move, and the skin consequently flexible and porous, and at the same time without tendency to putrefactive change. While the durability of wet raw hide is measured in days or weeks, Roman boots have been dug up which are hardly in worse condition than those which the tramp leaves, worn out, at the roadside. The methods employed by the tanner, though very similar in their effects, are so various that no single explanation, physical or chemical, will cover all of them; and often various actions are combined to produce the desired result.

The first general problem, then, regards the nature of the jelly state, which has many peculiarities. Van Bemmelen [1] and Bütschli [2] believed it to be a network or cellular structure of microscopic dimensions, and this view long held the field, but is now abandoned for that which regards it as a solid or semi-solid solution of which the colloid and water (or some other solvent) are the constituents. The question is still an open one whether the colloid is in the form of 'micellæ' (submicroscopic particles) or of large conjugated or polymerised molecules, but this is mainly a matter of terms, and at least it is clear that the mixture is so intimate that both constituents are within the range of molecular and electro-chemical forces.

The colloid most fully investigated in this relation is gelatine, which in its chemical constitution is almost identical with hide fibre, while its homogeneous character renders exact quantitative study much more possible. Soaked in water at laboratory temperature, it does not dissolve, but swells to a definite volume dependent to some extent on the particular sample and the temperature. When the temperature is raised above 25°, the jelly melts and becomes miscible in water in all proportions, though even when diluted considerably beyond its original equilibrium volume, it still 'sets' on cooling to a coherent elastic mass. Gelatine, both as jelly and solution, always shows a slight Tyndall effect, reflecting a beam of light sideways; but the ultramicroscope shows no defined particles. Arisz [3] has shown that the Tyndall effect increases with concentration and with lowered temperature, but without any break or sudden change at the setting point. The viscosity shows a similar increase, with no actual break, but a rapid rise at the temperature of gelatinisation, below which it speedily becomes too great to measure by ordinary methods. Both these effects are reversed on gradual heating, but there is a 'lag' in both directions, a cooling solution only acquiring its full viscosity and

[1] *Z. Anorg. Chem.*, 1896, 13, 304; 18, 15.

[2] *Untersuchungen über mikroskopische Schaume und das Protoplasma*, Leipzig, 1892. *Verh. des naturh.-med. Vereins zu Heidelberg*, 1892, N.F. 5, 28–41; *ibid.*, 42–43; *ibid.*, 1893, 89–102; *ibid.*, 1896, 457–472; *ibid.*, 1894, 230–292.

[3] *Kolloidchem. Beihefte*, 1915, 7, 22.

Tyndall effect after the lapse of considerable time, which may even extend to weeks, but below 60°, given time, the process seems completely reversible. Above 60°–70° some permanent change takes place (hydrolysis or depolymerisation) which results in lowered viscosity, Tyndall effect, and setting power. These facts are best explained by the hypothesis that below 60° the gelatine solution is one of molecules or small molecular aggregates, which, as temperature falls, gradually unite to form larger ones, and at the setting point unite to a complete molecular network analogous to a mass of tenuous crystals. Cases are known in which such crystalline masses closely simulate colloid jellies. Time is of course needed for this rearrangement, as it is for actual crystallisation, and owing to the size and comparative immobility of the particles, rearrangement is very slow. Kundt [4] has shown that under the influence of rapid flow at 18° (which is below the setting point) even very dilute and quite liquid solutions of gelatine show the polarisation effects of strain, while no such effect could be observed with glycerine or sugar solutions of much higher viscosity. The writer proposes to repeat these experiments at higher temperatures, but in the meantime it is clear that the viscosity of such solutions is not due simply to liquid friction, but includes an element of strain.

Proteids, among which gelatine must be included, are now known to consist of open or closed chains of amino acids, linked by the carboxyl group of one to the amino group of the next with elimination of OH_2. In closed chains, groups within a single molecule, forming terminal amino and carboxyl groups are also similarly united ring-structures. In this case the molecule is electrically neutral, and non-reactive till the ring is broken, while the open chains are amphoteric—basic by their terminal amino group and acid by their carboxyl. A very useful practical distinction is that ring proteids are unattacked by trypsin alone, while pepsin is able to open the ring.[5] Gelatine can be digested by trypsin, but collagen is only attacked by pepsin, hence the view, supported by other facts, that collagen is the ring or anhydride form of gelatine into which it is converted by continued boiling or by the action of acids or alkalies.

If gelatine (or hide fibre) be placed in dilute acid, it swells very much more than in water alone, and at the same time a considerable amount of free acid disappears (*i.e.*, is no longer capable of reddening methyl orange). The effect is most readily investigated with a strong monobasic acid such as hydrochloric acid. In this case the maximum swelling, which may reach an absorption of 50 c.c. of liquid for 1 grm. of dry gelatine, occurs at an acid concentration under 0.005 N, from which it rapidly falls in a curve of hyperbolic type as the concentration is increased, the equilibrium being completely reversible up to about 0.25 N, beyond which some secondary reaction, probably a further breaking up of the proteid chain, begins to take place. At the same time the total absorption of acid steadily increases with concentration in a curve which may be closely represented by the ordinary adsorption formula, $a=kx^{\frac{1}{p}}$ (where a is total acid, x the concentration of external solution, and k and p are

[4] *Wied. Ann.*, 1881, 13, 110.

[5] Plimmer, *Chemical Constitution of the Proteids*, Part II. p. 11 (Sec. Ed., Longmans, Green, & Co.). The statement seems to require confirmation.

constants) ; but which is really due to a complicated osmotic equilibrium which must be further explained.[6]

Gelatine, being amphoteric, acts as a very weak alkali in presence of hydrochloric acid, and forms a gelatine chloride, which like most salts is highly ionised (in fact to practically the same extent as hydrochloric acid itself). The base, however, is *very* weak, its ionisation being of the same order as that of water, and consequently the salt is largely hydrolysed, and can only exist in the presence of free acid. Thus gelatine base, gelatine chloride, and free hydrochloric acid are necessarily present in such a jelly in proportions determined by the concentration of the acid, and instead of a definite point of neutrality such as is given by a strong base, we have only a curve approaching, but never reaching, complete neutralisation. This is the explanation of the apparent indefiniteness of proteid compounds, which has led many chemists to deny the existence of definite proteid salts. By determining the hydrolysis curve and calculating the upper limit to which it tends, it is possible to calculate quite definite combining equivalents. Procter[7] in this way, on the assumption that gelatine had a second valency negligible at low acid concentrations, found a combining weight of 839, while Wilson,[8] from the same experiments, but regarding the apparent second valency as due to incipient decomposition or experimental error, found 768. It is not to be supposed, however, that these comparatively low weights represent the real complexity of the probably polymerised molecule in aqueous solution, but merely the smallest molecular division chemically possible.

It has been stated that the swelling of gelatine in acids is due to a complicated osmotic equilibrium, and that it reaches a maximum at a very small acid concentration, and is repressed if the concentration is increased. A similar repression is caused by the addition of any salt with the same anion to the outer solution, and as neutral salts have no decomposing effect on gelatine, the repression can be carried much further than with acid; thus a chloride jelly treated with sodium or potassium chloride is reduced to a horny mass. Seeing that the jelly is almost as permeable as water both to ionised and unionised salts and acids, it is hard to see how this repressive osmotic pressure is exerted. The following is the explanation :—

In equilibrium between a jelly and its external solution not only must all osmotic pressures be equally balanced, but, as has been shown by Donnan,[9] the electro-chemical condition must be fulfilled that the *products* of the concentrations of any pair of diffusible anions and cations common to both phases must be equal. Thus with gelatine chloride and free acid the chloridions multiplied by the hydrions must be equal in the jelly and the external acid. On the other hand, the osmotic pressures depend not on the *products* but simply on the *sum*

[6] It may be well to point out here that the 'adsorption formula' just quoted is absolutely void of theoretical basis, as regards adsorption, but is a mathematical expression which will closely represent any chemical or physical phenomenon which proceeds at a diminishing ratio. It is, for instance, the exact law of distribution of a solute between two immiscible solvents, in one of which its molecular complexity is p times that in the other.

[7] *T.C.S.*, 1914, 105, 320.

[8] *J.A.L.C.A.*, 1917, 12, 108,

[9] *Zeits. Elektrochem.*, 1911, 17, 572 ; Donnan and Harris, *T.C.S.*, 1911, 99, 1575.

of diffusible particles present. In the external acid the numbers of hydrions and chloridions are obviously equal, while in the jelly the chloridion of the gelatine chloride is added to the equal hydrion and chloridion concentrations of the free acid present, thus making the final concentrations of these ions in the jelly unequal. Now, as the sum of two unequal factors is always greater than that of two equals giving the same product, or, geometrically the perimeter of a square is always less than that of any other rectangle of equal area, and as the sides represent the osmotic pressure, while the area represents the product, it is clear that the two equalities cannot at once be completely fulfilled, but in electro-chemical equilibrium the osmotic pressure must be in excess and the jelly must tend to swell unlimitedly and finally to dissolve. That it does not do so is a consequence of its colloid nature, which depends on cohesive attractions drawing the colloid particles together to polymerised masses or to a continuous network, and which consequently opposes swelling and solution, while the diffusible ions are held to the colloid ions by electro-chemical attractions, and, as they cannot escape from the jelly, tend to drag it apart and dilute it by absorption of the external acid, from which they expel a part of its acid concentration. The equilibrium is therefore a very complex one, but finally depends on the excess of internal osmotic pressure being balanced against the internal attraction or cohesion of the colloid particles, both ions and molecules. For its mathematical discussion the reader must be referred to original papers by Procter and his pupils. It will, however, be obvious that as the external solution becomes more concentrated the proportion of absorbed acid (or salt) is increased, while that of gelatine chloride is limited to the quantity of gelatine present. The difference of concentration of hydrion and chloridion in the jelly is therefore diminished, and it contracts under the influence of its own internal attractions. Precisely similar considerations apply to the action of alkalies on gelatine. Ionisable salts are formed by combination of the base with the carboxyl group of the proteid, and the osmotic equilibrium is with the cation and OH instead of with the anion and H. Neutral gelatine, as an amphoteric body, of course ionises to a limited extent with water alone, and its dissociation constants are of the same order of quantity as those of the water with which it is in equilibrium. It is, however, slightly stronger as a base than as an acid, and consequently its neutral point of minimum swelling is slightly on the alkaline side. This has important bearings on manufacturing practice, the greatest flaccidity of the raw skin, which is required for the softest leather, being obtained in weakly alkaline liquids.

It has been pointed out by Donnan [10] that in consequence of the unequal distribution of positive and negative diffusible ions which has just been described, the surface of an acid or alkaline jelly in equilibrium has necessarily an electrical charge or potential, greatest at the maximum swelling, and such charges seem an essential condition of the colloid state. The surface is positive or negative according to whether the diffusible anion or cation is retained in the colloid. Thus gelatine and hide fibre are negative in alkaline and positive in acid solutions, and it will be shown later that this has an important bearing on the theory of leather manufacture.[11]

[10] *Zeits. Elektrochem.*, 1911, 17, 579.

[11] See below and Papers under 13.

Wilson[12] has extended these facts to a general theory of colloids and adsorption, showing that all surfaces must possess a potential due to unbalanced chemical forces on the surface, and therefore in a liquid containing electrolytes must condense ions or particles of the one sign on its surface, and repel those of the opposite sign; and also showing that surfaces must therefore be surrounded with a film of liquid of different concentration to the bulk, to which the same considerations and equations are applicable as to the absorbed solution of colloid jellies. For fuller mathematical treatment the reader is referred to original papers.

Some of the views just explained are so recent that their bearing on actual tanning processes has hardly had time to make itself felt in technical literature, and for its latest applications Papers by Procter and Wilson must be consulted,[13] but a brief summary may here be given.

As has been explained, the leather-hide, freed from epidermis, consists of a sort of felt of fibres of gelatigenous tissue, which are themselves bundles of finer fibrils cemented together by some substance nearly identical with, but somewhat more soluble than that of the fibrils themselves. Treated with dilute alkalies or acids, this cementing substance is more or less completely dissolved, and the fibrils themselves are swollen. Accurate chemical investigation of skin is complicated by this fact of structure, for while the free acid or alkali absorbed in the jelly of the fibre is subject to the mathematical laws which have been explained, the interstices between the fibres are also filled with external solution by capillarity, and no accurate means has been found of measuring the proportion between the two. Hide swollen in acid or alkali is tense and firm, and containing its liquid in jelly-form in the fibres only parts with it under heavy pressure; but when the fibres are dehydrated by neutralisation, the skin becomes 'fallen' or flaccid, and apparently much wetter, since the imbibed water is easily squeezed out. If in this condition the loose water is removed by soaking in alcohol or other dehydrating agents, the fibrils no longer adhere to each other, and a soft leather is produced, which, however, on again soaking in water, rapidly returns to its raw or 'pelt' condition.[14] If, however, a little stearic acid is dissolved in the alcohol so as to coat and partially waterproof the dehydrated fibrils, the leather at once becomes tolerably permanent. This led Knapp to the view that the process of tanning was merely an isolating and coating of the fibrils, and, though the explanation is incomplete, it unquestionably is part of the true one.

In order to make a soft leather, it is therefore necessary to have the skin in a flaccid or unswollen condition, and, assuming that it has been swollen by lime, this is brought about essentially by neutralisation. The older processes depend on fermentations of bran, pigeon and dog dung, and the like, and just as liming serves the several purposes of swelling the hide, loosening the hair, and partially saponifying the fat, so these fermentation processes not merely neutralise the lime by weak acid, or salts of weak bases, but remove cementing substance

[12] *Jour. Am. Chem. Soc.*, 1916, **38**, 1982.

[13] Procter, *Koll. Beihefte*, 1911, **2**, 270; *T.C.S.*, 1914, **105**, 313; and Wilson, *T.C.S.*, 1916, **109**, 307; 'Swelling of Colloid Jellies,' *J.A.L.C.A.*, 1916, **11**, 399; and Burton, D., 'The Swelling of Gelatinous Tissues,' *J.S.C.I.*, 1916, **35**, 404.

[14] Knapp, *Natur und Wesen der Gerberei*, Braunschweig, 1888; Meunier and Seyewetz, *Coll.*, 1912, **11**, 54.

from the fibres by the digestive effects of bacterial enzymes, and complete the emulsification of fats and the solution of residues of the epidermis. It is obvious that the attainment of all these varied results by an artificial preparation is no easy matter, but an approach to a complete solution has been made by J. T. Wood[15] (followed by Dr. Röhm, who has improved working details), by a mixture of ammonium chloride and pancreatic digestive ferments, which for many purposes fulfils its object better and much more safely than the old materials. The tryptic ferments dissolve the epidermis residues and cement-substance, but scarcely affect the collagen fibres (v.s.). They also facilitate emulsification of fats by reducing the surface tension between jelly matters and the liquid, while the presence of free ammonia and excess ammonium salts regulates the hydroxyl concentration to something near the alkalinity required for minimum swelling (v.s.). Possible improvement lies in the direction of the discovery of new enzymes, and of suitable weak bases and 'buffer' substances, to give the precise degree of solution and of acidity or alkalinity required for the various leathers. For firmer leathers the use of weak acids regulated by excess of their salts produces a sufficient degree of neutralisation and flaccidity.

We must now consider the conversion of the still raw and very putrescible skin into permanent leather. We have seen that this can be accomplished by dehydrating the fibrils without allowing them to adhere (v.s.), and by coating them with water-resisting substances; but it is known that similar effects of an even more permanent character can be produced by reagents (notably formaldehyde and bromine) which act chemically on the collagen fibre, rendering it insoluble in water, but which in their nature cannot deposit any exterior coating such as was assumed by Knapp. We must therefore conceive the process as being in most cases a combination of both chemical and physical effects, of which sometimes one, sometimes the other, preponderates, according to the method employed. We have also to consider reactions which from their colloid character differ somewhat widely from those of free ions to which the term 'chemical' is generally applied. It is therefore best to proceed from simple cases of which definite explanation can be given, to the complex in which more than one sort of reaction takes place.

Knapp's alcohol leather, in which a material is produced with all the physical characteristics of a complete leather by simple dehydration of the hide fibres under conditions preventing adherence, has been already mentioned (v.s.). The theory of acid swelling has also been described, and it has been shown that as the anion concentration of the external solution is increased the difference of osmotic pressure between it and the jelly which causes swelling is diminished without limit, and the fibre contracts by its internal attractions. This fact is applied in the process of 'pickling' which is principally employed in the preservation of sheepskins before tanning. The skins, after unwooling, are treated in a bath of dilute acid, generally sulphuric, to which some salt is added to prevent excessive swelling, and are then transferred to a saturated solution of common salt. The dehydration of the fibre is very great—the skin becomes thin and flat, and can be preserved almost unlimitedly in the wet condition; and if dried out and loosened by a little mechanical

[15] Wood, *Puering, Baling and Drenching*, Spon, 1912, p. 186.

stretching, forms a very perfect white leather, which, however, softens and swells at once in water through the removal of the restraining salt. It is not essential that the acid should be a ' strong ' one. Skins pickled with formic acid and salt by Mr. Seymour-Jones were sent on a voyage up the Amazon, and returned in perfect condition. It is obvious that if a skin swollen with some acid other than hydrochloric be subsequently treated with salt, a quadruple equilibrium results, most of the proteid salt being converted into chloride by the great excess of sodium chloride, with the formation of the sodium salt of its acid, each proteid salt being balanced against its own anion in the external solution. In a direct experiment with gelatine formate almost the whole of the formic acid was replaced by hydrochloric. It is probable that the so-called ' free ' hydrochloric acid in the gastric juice has been liberated in this way, and really exists as a salt of some weak colloid base.

In the ordinary processes of production of ' alumed leathers ' it is impossible to work without considerable addition of salt, and the process is largely a pickling one, the hydrolysed acid of the aluminium salt combining with the skin and leaving a basic salt which is also absorbed, the quantitative relation between the two independent actions depending on the relative concentrations. If, instead of alum or normal aluminium sulphate, a basic alumina solution is used, salt can be reduced or dispensed with, and the tanning action depends less on pickling and more on the fixation of alumina. What has been said about alumina tannage applies with little variation to tannage with chrome and iron salts.

As regards the fixation of alumina and chrome, there is little doubt that in the first instance it takes place in the form of basic insoluble salts and is largely physical. The more basic a solution of these metals and the more readily and completely it is precipitated by the withdrawal of a further portion of acid, the more heavily it tans. If we imagine a normal salt to diffuse into the skin, and its acid to combine with the amino group of the proteid, then the remaining insoluble basic salt must remain precipitated in and on the hide fibre. Whether this is the final stage may be doubtful—Wilson, in a recent Paper on ' Theories of Leather Chemistry,'[16] suggests that ultimate combination takes place with the carboxyl group, and this view seems well in accordance with known facts. A. L. Lumière[17] has shown that the maximum amounts of chrome and alumina which can be fixed by gelatine accord well with this view; and Wilson points out that if, as he supposes, the ultimate gelatine molecule is monacid and monobasic, a divalent ion such as $Ca^{\cdot\cdot}$, joined to two gelatine molecules, should exert only the same osmotic pressure as the monovalent $Na^{\cdot}$, and hence its swelling effect should be much less as is known to be the case; while the trivalent $Al^{\cdot\cdot\cdot}$ or $Cr^{\cdot\cdot\cdot}$ should swell still less and be yet more easily repressed; and that therefore chrome or alumina gelatinates, if they exist, should be very stable and insoluble compounds. It is well known in practice that change in the direction of stability gradually takes place on storing or ' ageing ' alumed leather, and probably the same is true of chrome, though not so easily demonstrated.

Vegetable tannage appears to be of a more colloidal or physical character than that with alum or chrome. Tannins, like the proteids, appear

[16] *J.A.L.C.A.*, 1917, **12**, 108.
[17] *Brit. Jour. Phot.*, 1906, **53**, 573; Abst., *J.S.C.I.*, 1906, **25**, 770.

to form colloidal, rather than true ionic solutions, and the particles are negatively charged, going to the anode in electrophoresis. Whether the change is due to ionisation or to the fixation of an electrolyte ion is immaterial for our purpose. The gelatinous fibres, as we have seen, take a positive charge in acid, and a negative one in alkaline solutions (v.s.). Hence in faintly acid solution, which produces the strongest positive charge, they attract and precipitate the tannin particles, while in alkaline solution no tannage takes place, and in those too strongly acid, the tannins themselves are precipitated.[18] In fact, such colloid precipitations due to electric charges do not seem to differ in principle from ionic reactions, though owing to the varying size of the particles and of their charges they are less definite and quantitative. Whether ultimately any closer combination with the fibre ensues, as is suggested in the case of mineral tannages, remains for the present uncertain, but in long-continued tannage there is a further deposition of difficultly soluble matters on and between the fibres by forces generally called 'adsorption.' We may thus divide vegetable tannage into two stages, in the first of which the tannins combine electrically or chemically with the fibre and render it insoluble, and in the second matters are deposited upon it which add to the weight and solidity of the leather; but of course the two stages overlap in time, and the different qualities of leather produced by different tannages are largely due to their relative proportion, and the amount of precipitable matter which the tanning materials contain. It does not appear that the same affinities are saturated in mineral and vegetable tannages—chromed leather will fix as much vegetable tannage as raw hide, and *vice versa*; and corresponding differences occur in their behaviour to dyestuffs.

Besides the mineral and vegetable leathers there is a third class which demands consideration. If raw skins are fulled with oxidisable oils, their water is gradually expelled and replaced by the oil, and if the skins are now allowed to oxidise (which they do with considerable liberation of heat and of acryl aldehyde and other volatile products), and are then freed from unfixed oil by pressing and subsequent washing with alkaline solutions, such leathers as 'chamois,' 'wash-leather,' 'buckskin,' and 'buff-leather' are the result. Oil leathers, like chrome leathers, are very resistant to hot water, and also to hot soap or alkaline solutions, and may even be shrunk or 'tucked' to increase their thickness and solidity by dipping in these liquids at boiling temperature. Their resistance to hot alkaline solutions, in which all oxidised oil products are soluble, proves that something more has occurred than a mere coating of the fibres with oils, but a full explanation has not yet been given. Since aldehydes are known to produce insoluble conjugated products with hide fibre, the explanation that acryl aldehyde (derived from the glycerine by dehydration) was the active agent was a plausible one, but is negatived by the recent knowledge that equally good leathers can be made with the free fatty acids alone. This, however, does not altogether disprove the aldehyde theory, since the unsaturated oils which alone will chamois are apt on oxidation to break at a double linkage with the production of higher aldehydes. Another possibility is that these oils, which are more or less colloid, form emulsions of which

[18] *T.C.S.*, 1916, 109, 1329.

the particles are electrically charged, and which combine with the fibre in the same way as the tannin particles may be supposed to do, though probably with an opposite charge (v.s.).

The oil squeezed out and known as *moellon* or *dégras* is a natural emulsion, and finds wide use in leather-dressing for the 'stuffing' of light leathers. This stuffing, the primary object of which is to lubricate the fibres and make the leather supple and water-resisting, may in many cases be also regarded as a supplementary and partial oil-tannage. The fats are applied to the moist leather either by hand as a pasty mixture of oils and harder fats, or in a melted state in a heated rotating drum. In the first method the main effect of the harder fats is to retain the mixture on the surface until the oils are absorbed. The water in the leather lowers the surface tension between oil and leather at the interface, and as the water dries out the oil replaces it by capillarity, leaving the harder fats outside. The surface tension of the various fats with regard to water and their consequent easy emulsification is thus of great practical importance.

A third way of applying fatty matters to leather much used for chrome and other light leathers, and called 'fat liquoring,' consists in drumming the skins with a prepared emulsion, which at first was the alkaline liquor from the washing of oil-leathers, but is now usually an artificial mixture of oils and soaps, though occasionally acid emulsions are employed. It has been found that sulphonated oils, especially castor and fish oils, have extraordinary emulsifying powers even on hydrocarbon oils, and the writer has examined a commercial product containing 80 per cent. of mineral oil, which yet was perfectly and spontaneously emulsifiable when poured into water. The question of surface tension at interfaces and against solid surfaces is one of much technical importance, and probably its effect on adsorption is greater than that of the Willard Gibbs law that 'substances which lower surface tension accumulate on that surface.' The action of protective colloids on metallic sols has been explained as due to the fact that the surface tension of the medium at the metallic surface is greater than the sum of the tensions of the medium and the metal with regard to the protective colloid, which therefore spreads in a thin film between them. This coating of the metal by the colloid is of course an adsorption; and a similar action may account for many cases of the latter which are called 'anomalous,' that is, to which the Willard Gibbs law does not apply.

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GENERAL REVIEW AND BIBLIOGRAPHY OF DYEING.

By P. E. KING, *Lecturer in Dyeing, University of Leeds.*

The Present State of Development of the Theory of Dyeing, with special reference to colloidal and electrical hypotheses and phenomena leading thereto.

In the present stage of the evolution of an adequate theory to explain the phenomena of the dyeing process, four somewhat conflicting theories prevail :—

The mechanical or physical theory,
The chemical theory,
The colloid-diffusion and adsorption theory,
The electrical theory.

The two former were long the cause of energetic discussion between their respective upholders, the two latter have been developed since the beginning of the present century, and are to be looked upon, less as parallel theories to the first two, than as more scientific attempts to supplement and correlate, in the light of later physico-chemical discoveries, the phenomena observed and partially explained by the older theorists.

The upholders of the mechanical theory[1] looked upon it merely as an adsorption phenomenon, of the dyestuff particles in the fibre; the second group took for granted a chemical combination between fibre and dye. The holders of the first view based themselves primarily on the analogy which subsists between dyeing and the absorption of dyes by animal charcoal. More modern investigations by Justin-Mueller, however, indicate that pure carbon absorbs only very little dyestuff. The decolourising effect of charcoal is connected with the presence of organic nitrogenous compounds, which are produced by the combustion of protein substances. The upholders of the chemical theory of dyeing, which may be described as the salt-formation theory, base their views upon the fact that the fibres, especially wool and silk, which by hydrolysis give amino-acids, contain salt-forming groups and produce actual salts with the dyestuffs, which, as is well known, contain acid and basic groups.

At present the most prominent upholder of the purely mechanical

[1] P. Sisley, 'Augenblicklicher Stand unserer Kenntnisse über die Theorie der Farbung,' *Chem. Zeit.* 1913, 1357, 1379.

theory is G. von Georgievics.[2] He has a long line of predecessors, from the earliest dyeing theorists of the first half of the 18th century, Hellot,[3] Dufay,[4] Macquer,[5] and Le Pileur d'Apligny,[6] down to Walter Crum,[7] Persoz, Engel, and Napier. He rejects categorically the theory of chemical combination between dye and fibre in the case of wool, on the grounds that such indifferent substances as glass beads, kaolin, and various other inorganic substances may be dyed in exactly the same way. He objects in details to O. Witt's theory of 'solid solution' (of the dyestuff solute in the fibre solvent) by combating each of Witt's statements from experiments of his own. His theory of the dyeing process is that the dye particles are in a state of adhesion on and in the fibre, and neither of solution nor chemical combination; the same he considers to be true of the various mordants. But this 'adhesion' is, he says, analogous to capillary attraction, to the adhesion of solute to solvent, and to that exerted, for example, by glass on a liquid which 'wets' it, and such forces as these, he admits, lie on the borderline between chemical and physical forces. A very similar conclusion had been drawn before by H. v. Perger,[8] L. Hwass,[9] and G. Spohn.[10]

Georgievics admits that basic dyestuffs when dissolved in water are dissociated, and that if the base has an attraction for a substance, a coloured body will be formed when the two are brought together. As evidence for the physical and against the chemical nature of dyeing, he relies chiefly on various forms of Henry's law of distribution.

He states from his experiments that in the majority of cases dyeing takes place according to the equation

$$\frac{\sqrt[x]{C_s}}{Cw} = \text{constant},$$

in which C_s denotes the colour taken up by the fibre, Cw that left in the bath and x indicates the affinity of the colouring-matter for the fibre. In some later experiments[11] with indigo extract and picric acid on wool and methylene blue on mercerised cotton, he states that dyeing proceeds according to the equation

$$\frac{\sqrt[x]{C \text{ dyebath}}}{C \text{ fibre}} = K$$

where x may be equal to one or greater than one and its value depends upon the temperature and additions to the bath. The rule only holds within certain limits of concentration of the dyebath, comparatively more colour being taken up from dilute than from concentrated baths.

[2] *Mitteilungen des K.K. Gewerbemuseums in Wien*, pp. 165, 205, 349 (1904), p. 345 (1905). See also *Journ. Soc. Dyers and Col.* 1895, pp. 79 and 121.

[3] 1734, *L'art de la teinture des laines et des étoffes de laine.*

[4] 1737, *Traité sur la Teinture, observations physiques sur le mélange de quelques couleurs à la teinture.*

[5] 1763, *L'art de la teinture de la soie.*

[6] 1776, *L'art de la teinture des fils et étoffes de coton.*

[7] 1843, *Journ. Chem. Soc.* 16, 1, p. 404.

[8] 'Einige Farbersuche,' in *Farbenzeitung*, 1890–1.

[9] *Farbenzeitung*, 1890, pp. 221, 243.

[10] Essay, 'Zur Erkenntnis des Farbevorganges' in *Dinglers' Polytech. Jour.* 1893.

[11] *Journ. Soc. Dyers and Col.* 1904, p. 105.

From his experiments Georgievics considers he has proved beyond doubt that the dyeing process takes place according to a definite physical law in the case of acid colours on animal fibres and salt colours on cotton. He uses Henry's law very indiscriminately and alters it to fit his figures.

The earliest mechanical theorists had been content with the theory that the dye particles from the solution wandered by endosmosis into the 'pores' of the fibres and were there fixed by the formation of an insoluble 'lake' with the mordant. This being done in a hot bath, the contraction of the pores on cooling, aided by a possible astringent action of the various mordants, held the dye particles fast. The first investigator to suggest adhesion of dye particles to the surface of the fibre was Macquer[12] in 1768, followed by Berthollet,[13] Thomas Henry,[14] Bancroft,[15] and finally Walter Crum,[16] the greatest of von Georgievics' predecessors, who defined this (purely physical) adhesion as 'catalytic force' and insisted on the analogy between the dyeing process and the absorption of gases, salts dissolved in liquids and colouring matters, in an unchanged form, by wood-charcoal and bone-black. Crum also points out the capillary attractive force of fibres, in common with other porous bodies. So well reasoned were his theories that the upholders of the then extremely vague and nebulous chemical theory felt themselves impelled to greater clarity and more logical statement of their point of view.

The title of 'first chemical theorist' is given to Bergmann,[17] who, in an essay on indigo, suggests that the wool extracts the whole of the indigotine disulphonic acid from the bath because it has a greater 'affinity' for it than the latter. This vague 'affinity' satisfied Berthollet, Henry, and Chaptal, but it was left to Chevreul,[18] the head of the Gobelin Dyeworks in Paris, to speak the first clear words on the nature of this 'affinity' in his 'Mémoire' of the year 1834. He divides dyes into chemical compounds, simple mixtures and substances that partake of the nature of both. Then, investigating those dyeing processes which appear to lead to chemical combinations, he says: 'Chemical combination is analogous to salt formation,' but the combinations between fibre and dyestuff are looser and evolve less heat than is observed in the case of acid reacting with base, and the combining proportions are not always constant. In dyeing, moreover, he recognises a 'contact-effect,' adhesion, which he places in a position next to affinity in importance, and calls 'capillary-affinity'; his conclusion is that there are molecular forces at work between bodies in contact, which slowly combine. Dyeing will not take place unless there is a greater affinity between the fibre and the dye than between the dye and its solvent, and in judging of the probable result it is necessary to take into consideration the water, with dissolved acids, bases, or salts; dyestuff; fabric, and one or more mordants of more or less complex character. That one fibre dyes better than another in the same bath he explains by the principle of 'elective affinity,' which at that time so greatly exercised the minds of the students of the infant science of chemistry.

[12] *Dictionnaire de Chemie*, article 'Teinture.'
[13] 1791, 1804, *Éléments de l'Art de la Teinture.*
[14] 1790, *Nature of Colouring Matters.*
[15] 1794, 1813, *Philosophy of Permanent Colours.*
[16] *loc cit.*
[17] 1776, *Mémoires des Savants Étrangers*, t. 9.
[18] *Mémoires de l'Académie des Sciences*, 1853, 1861. *Cours de Chemie appliquée à la Teinture*, 2me partie, 1838–1864.

Chevreul deserves honour not only for the pioneer quality of his statements, but also for the detailed tabular accounts of his experiments, which gave a stimulus to other investigators.

He was quickly followed by F. F. Runge [19] who confines his researches to cotton, discussing first the 'combat' between the water of the bath and the fibre for possession of the dye, and thus explaining the decrease in rapidity of deposition as the bath nears exhaustion. Mordants he conceives to be substances which eagerly combine (enter into) the fabric to form a substance that in its turn combines with the dye.

Persoz [20] postulates an attraction between the fibre and dye particles analogous to inter-molecular forces, but does not suggest true chemical combination between dyes and fibre. In 1856 F. Kuhlmann drew attention to the nitrogenous nature ('azoted fibres') of the fibres which readily absorb dye, experimenting with pyroxylin and cotton. He suggests that the part played by capillarity and adhesion in dyeing is subordinate if important, and also makes the remark that 'a chemical change which results in a change of dyeing-capacity may often be a mere re-grouping of molecules.' J. B. Schlossberger [21] follows with a little more leaning towards the physical theory. P. A. Bolley [22] reverts, after very careful research with the microscope into the place and nature of the deposition of the dye on the fabric, to the physical theory, finding that the deposition is only on the surface with silk and cotton, though partly within the wool fibre. His experiments finally lead to the conclusion that the absorption of the dye, with or without mordant, is a surface phenomenon entirely analogous to adsorption of charcoal, and that the use of the mordant is merely to form lakes. But the discovery of aniline colours in 1856 by Perkin, and the rapid spread of inquiry into their nature and application, emphasised the trend of opinion in favour of the chemists. Schutzberger [23] pointed out that in the dyeing of wool with aniline colours there was necessarily chemical action, usually between dyestuff and mordant, but does not suggest that the fibre in any way enters into the reaction; he looks on fibres as porous bodies, carriers of the dye. Again the physicists prevailed, until E. J. Mills [24] reported experiments in the dyeing of silk red from a colourless rosaniline solution, which he took to prove that the silk actually entered into combination with the dissociated colourless rosaniline base. The observation that wool is dyed red from a colourless solution of rosaniline base was first pointed out by Jacquemin in 1876. Mills gives careful tables showing the laws governing the rate of absorption of colour from a cold bath, also of various acid and basic solutions, and finally for the result of dyeing from mixed dye-baths.

R. Meyer,[25] on the subject of microscopic research into printed cottons, doubts whether the fibre enters into composition of a compound with the dye or acts as a containing vessel for the latter; he considers that the essential factor in true dyeing is that the dye or the materials which produce it in the bath should penetrate the fibre, and inside it be changed

[19] *Farben Chemie*, Pt. 1, 1834, Pt. 11, 1850.
[20] 1846, *Traité de l'Impression.*
[21] 1857, *Lehrbuch der organischen Chemie.*
[22] 1859, *Kritische und experimentelle Beitrage zur Theorie der Farbere Journal für praktische Chemie.*
[23] 1868, *Traité des Matières colorantes.*
[24] *Journ. Chem. Soc.* 1883, 144; *Journ. Soc. Chem. Ind.* 1889, 263.
[25] 1883, *Berichte.*

to an insoluble form. He, however, in 1895, admits that with animal fibres dyeing is a chemical process. The researches of P. Richard [26] into the nature of wool and silk led him to assert the existence of an amido group in these substances which can be diazotised and the resulting diazo compound coupled with phenols &c. At the same time, by decomposition of the diazo compound, a hydroxy group is formed which can be coupled with diazo compounds.

Champion's discovery of lanuginic acid being published, Knecht [27] now turned his attention to this in a long series of researches that have finally confirmed his position as leader of the purely-chemical faction. In 1888 he showed that, having prepared lanuginic acid either by Champion's method or by dissolving wool in barium hydrate solution, precipitating the barium with carbon dioxide and from the filtrate precipitating the acid with lead acetate, then removing the lead with sulphuretted hydrogen and evaporating the filtrate, the resultant substance gave brightly coloured precipitates with dye solutions of acid and basic dyes and also with solutions of metallic salts. Comparing this with the facts observed: that wool and silk absorb and hold with a tenacity which will not yield even on boiling acids and alkalies; that they also absorb dye-bases from neutral baths, leaving the whole of the acid from the dyestuff in the bath as ammonium salt; he deduces that definite chemical compounds must be formed between the colour-base (or under given conditions colour-acid) with some break-down products of the wool or silk of the nature of lanuginic or sericinic acid. With acid colours, the action of the acid produces in the fibre a substance capable of forming lakes with the acid colouring-matter. The behaviour of the fibre in presence of great excess of substantive dye in some experiments even shows the probability of combinations according to the law of multiple proportions. Knecht [28] undoubtedly proved that in dyeing wool with a series of acid colours belonging to the same homologous series the amount of colour taken up was in exact proportion to their molecular weights; hence the laws of chemical combination are obeyed.

These convictions of Knecht have been continuously combated by von Georgievics and the physicists, but a series of investigators reported experiments which corroborated Knecht's observations. L. Vignon [29] tested for the amount of heat evolved in the absorption of acids (sulphuric, hydrochloric, stannic) and alkalies respectively by silk, wool, and cotton, and found that the first fibre evolves the greatest heat, even during absorption of salts. Cotton only evolves heat with strong acids or alkalies, and then only feebly; this he explains by the fact that cotton has no nitrogen (citing empirical formulæ),

$$\text{silk} = C_{141}H_{222}N_{48}O_{56}\,;\ \text{wool} = C_{88}H_{149}N_{27}S_3\,;\ \text{cotton} = C_6H_{10}O_5.$$

and that cotton previously treated with ammonia will react evolving heat. He obtains a substance by treating cotton with ammonia, which contains nitrogen, and this substance possesses greater dyeing powers, but in the opinion of the writer this compound is far more likely to be a degradation product of cotton. Wool and silk he knows to be capable of

[26] 1884, *Soc. Ind. de Mulhouse*, 'Aufklärung der chemischen Konstitution de Wolle.'

[27] *Journ. Soc. Dyers and Col.* 1888, p. 72; 1889, p. 71.

[28] *Ibid.*, 1904, p. 242.

[29] *Comptes Rendus*, 1890.

acting either as acid or as base under determining conditions, and postulates a definite acid or basic character both in the fibre and in the dyestuff before true dyeing can take place (dyestuff here being taken to mean the system solvent plus solute dye plus mordant). In 1893, criticising the new Witt theory, he emphasises the chemical nature of his own hypotheses as being far more 'rational and in accord with facts.' That there is no clearly demonstrable adhesion to the law of multiple proportions he considers to be no unanswerable argument; the fibre molecules are complicated and large in comparison with those of many dyes. Vignon on this and other occasions pointed out the dissociation of dye-solutions in presence of the fibre; the constitution of dyes like Congo red (R or =N – N=) that possibly makes them capable of the direct dyeing of cotton by combination with the cellulose. Finally, he admits the great value of the physical structure of the fibre in dyeing, its $\frac{\text{surface}}{\text{volume}}$ coefficient being so large that it acts as a porous body. As did Zacharias later, he admits of two actions of the fibre: porosity with capillarity, and (usually) chemical combination. Knecht[30] also showed that hydrolytic dissociation played a part in dyeing and that there was an intimate connection between the dissociation of a colour and its dyeing power.

L. Hwass and G. Spohn[31] adduce experiments in favour of the mechanical deposition theory, the latter insisting on deposition pure and simple, conditioned by molecular forces, and giving as evidence the microscopically visible crystals of lead chromate and manganese bistre, which at a distance of 60$\mu\mu$ one from the other give the illusion of homogeneous colour to the naked eye, but are separately and sharply deposited, some within, some upon, the fibre. He, like von Georgievics, refuses to admit of any chemical combination, since inorganic and unaffected matters like asbestos can be dyed just like animal and vegetable fibres, but Hwass admits the possibility of such combination (*e.g.*, silk saturated with iron hydroxides). He looks on dyeing as dissociation phenomena; dyestuffs readily dissociate, and the fibre acts towards the dissociated solute merely as would a thread hung in a saturated alum solution: it receives and encourages the deposition of insoluble bodies (the colour radicle or its hydrate) and rejects soluble. He is attracted to the solid solution theory of Witt (*vid. sub.*) as being the best statement of such phenomena of selection. The appearance of von Georgievics in the arena now so thoroughly stated the case for the purely mechanical deposition theorists that no further citations need be made from the researches of his disciples to bear out his theories.

Meanwhile, in the hands of C. O. Weber,[32] W. P. Dreaper,[33] Rosenstiehl, Gnehm and Rotheli,[34] A. W. Hallitt,[35] A. Reychler,[36] Prudhomme,[37]

[30] *Journ. Soc. Dyers and Col.* 1898, p. 59.
[31] *loc. cit.*
[32] *Journ. Soc. Chem. Ind.* 1894, p. 120.
[33] *Ibid.*, 1904, p. 111; 1905, pp. 118 and 136.
[34] *Journ. Soc. Dyers and Col.* 1898, pp. 190 and 215.
[35] *Ibid.*, 1899, p. 30.
[36] *Bull. Soc. Chim. de Paris*, 1897, p. 449.
[37] *Rev. Gen. de Matt. Col.* 1900, p. 184.

and Knecht himself, the chemical theory developed, and widened its horizons until it merged into the view that any dyeing process is necessarily dualistic: that some physical cause of deposition, be it (1) purely mechanical adhesion or (2) intermolecular diffusion analogous to the interdiffusion of any two solutions, with miscible solvents, until a state of equilibrium is reached, or (3) attraction of an electrical nature due to contact-difference of potential in the presence of a solute hydrolysed or ionised, must accompany any postulated chemical combination of dye and fibre. The fundamental theories governing the chemical combination of fibre and dye are twofold: (1) All dyestuffs have either acid or basic properties or represent salts of acids or bases, (2) these dyestuffs combine with the animal fibres, especially wool, by virtue of the amphoteric nature of the latter. In the case of cotton, although the process is generally looked upon as being of a mechanical character, it is quite conceivable that a chemical action may sometimes occur.[38]

If cotton be rendered more acid, *i.e.*, by the formation of oxy-cellulose or nitro-cellulose, the fibre shows a marked affinity for basic colours. But nitrated or acetylated cotton has lost its affinity for direct colouring-matters. More evidence in favour of the Chemical Theory was advanced by Fort[39] in a series of papers in the 'Journ. Soc. Dyers and Col.' He constructed a theory to explain the taking up of acid dyes by materials which are able to effect combination with acids and supported this theory by a large number of experiments.

The first steps towards a clear and adequate explanation other than that of chemical combination of the phenomena of absorption by the fibre or a dye from its aqueous or alcoholic solution were made by A. Muller Jacobs.[40] He bases his researches upon the known facts of diffusion of gases, of one liquid through another, and of crystalloid solutions through membranes that prevent the diffusion of colloids. Researches in the last-mentioned diffusions had been first published by Thomas Graham[41] in 1861-1864. Muller Jacobs divided the 'attraction' between the phases of a disperse system into 'hygroscopy,' 'capillarity,' and 'imbibition' between solids and liquids, all based on the phenomena of endosmosis. He is aware that even colloids will diffuse if the membrane be suitable (this confirmed in 1912 with great accuracy by Zsigmondy and Siedentopf) and applies this to dyeing. Many dyestuffs, whose colloidal nature is known, will diffuse into and colour a parchment membrane, but will not stain the surrounding solvent. Some enter into the cell wall, some appear to be fixed upon it. Now, in dyeing the aim is either to fix this interpermeated colloid by a mordant which will turn it to an insoluble precipitate, still within the fibre, or to cause the endosmosis of such large molecules of the colloid dyestuff that it will not readily diffuse out. Silk and wool have small interstices in their membranous structure: an 'animalising' process is any which so closes up the large interstices of the cotton fibre that it will act in the same way. There is no need to postulate any entry into chemical combination on the part of the fibres (*e.g.*, with the colourless rosaniline solution). Heating is of value because it expands the pores of the fibres—here he reverts a century to the pure mechanicists of the infancy of the science—

[38] See Knecht, *Manual of Dyeing*, vol. 1, p. 19.
[39] 1913, p. 269; 1914, p. 5; 1915, pp. 80, 96, and 222; 1916, p. 33.
[40] *Textile Colorist*, 1884 and 1885.
[41] *Philos. Transact.* 1861–1864.

and also because it favours the combination of the dye plus mordant into insoluble lakes.

O. N. Witt's [42] theory of selective solution and of solid solution was the next step. The phenomenon of solid solution was first noticed by Van 't Hoff [43] in 1890, as an explanation of the formation of alloys by the solution of one solid metal in another. Witt's application of this to dyeing was, it must be remembered, put forth as a 'working hypothesis,' which appeared to its formulator as being capable of explaining many observed facts, and which might at least serve as starting-point for a more adequate theory. His initial objection to the terminology 'substantive' and 'adjective' colours is, that the success of the dyeing process depends on the fabric as well as on the dye: one fibre will not take all dyes nor will one dye colour all fabrics. This is not, he says, explained by chemical combination, but by choice of solvent, the fibre is a better solvent for the dyestuff than is the water of the bath, and absorbs the colour in the same way as ether will take iodine from its brownish water-solution and form a violet layer, or as ether absorbs resorcin from its aqueous solution, whereas benzol will not, save in minute quantities, though resorcin is soluble in benzol. Keratin and fibroin are very good solvents, cellulose a poor solvent, for colours; but no dyestuff can be truly insoluble in the fibre, or it would wash out. He insists that the colour on the fibre is the colour of the dissolved, not the solid dye, *e.g.*, magenta dyes red. not metallic green, and fluorescein dyes fluorescent, though it only fluoresces in solution. So illuminating was the theory at first glance that it found many upholders: P. Sisley, W. H. Perkin, Michaelis, Cross and Bevan, and at one time Dreaper; and it was only when von Georgievics, Biltz, Freundlich, and Walker and Appleyard made exhaustive researches into the laws governing colour adsorption (*e.g.*, that Henry's law is not obeyed, unless totally unfounded assumptions are made as to the molecular constitution of the absorbed dye) that the inadequacy of the theory was demonstrated.

Cross and Bevan in 1910 still insist, from the pure transparency of the jute-fibre when dyed dark blue with a mixed solution of potassium ferricyanide and ferric chloride, that this is a case of 'solid solution' [44] and Sisley [45] in 1913 claimed that 'Berthelot's law' on the distribution of a dissolved substance between two immixable solvents holds good in dyeing silk with certain acid dyestuffs, and quoted his experiments to show the analogy between the extraction of picric acid from its aqueous solution by silk on the one hand and by organic solvents such as benzene or amyl alcohol on the other hand, the action in both cases being accelerated by the presence of a mineral acid, because it is found that fully ionised dyestuff, *i.e.*, one in very dilute aqueous solution, will not come out of its water solution on to fibre or into organic solvents, and the addition of an electrolyte diminishes the ionisation coefficient and the solubility of the dyestuff in water. C. O. Weber [46] likewise believes that benzidine colours go into solid solution in the cotton fibre, the fastness of the colour to washing being inversely proportional to the diffusion-coefficient of the dye. The then extant theories of colloidal solution were first applied

[42] 'Theory of the Dyeing Process,' in *Farbenzeitung*, 1890–1.
[43] *Zeitschr. f. phys. Chemie* (1890), **5**, 322.
[44] See also *Journ. Soc. Chem. Ind.* 1893.
[45] *loc. cit.*
[46] *Journ. Soc. Chem. Ind.* 1894, p. 120.

by F. Krafft[47] to the theory of dyeing. His summary of the facts then known is this: a colloid solution or system contains the solute in molecular form; the molecules are large in mass and volume, and tend to form systems rotating round one another. When the gel coagulates these spheroid forms become rigid—the solid is not 'amorphous' but 'globomorphous' (this is not true unless the disperse phase occupies no more than 74 per cent. of the total volume of the sol;[48] above 74 per cent. the globules become flattened to dodecahedra, with walls, of increasing tenuity, consisting of the continuous phase—but such fine walls are rare save in the soaps). Krafft goes on to state that in dilute solutions the soaps are hydrolytically dissociated, but the constant interchange of +ve and −ve ions causes the neutral reaction to persist and the solution to remain 'clear.' His proof of dissociation is that the melting-point is that of stearic acid, not of sodium stearate. Hence Krafft's theory of the dyeing process is that it consists in the deposition of colloids in or on the fibre in the form of globules or membranes, very plastic, which (like the soaps) have the power of clinging to solid bodies. Dyes which have a small molecular weight must be presented to the cotton fibre in the form of colloidal compounds with a mordant, which is in itself always a colloid, to form colour lakes. Many dyes are colloids in water and not in alcohol; the substance is hydrated and forms immense molecules Colloid solutions of iron hydroxide, aluminium chloride, *i.e.*, in water, will all form colour lakes which 'fall out of solution' (*i.e.*, coagulate) at 0° C. (see Zsigmondy's experiments in freezing sols). Their tough, plastic, clinging nature all makes for good dyeing, *e.g.*, alizarin red in presence of a fatty acid of low melting-point forms a colloidal membranous deposit, Turkey red. Direct dyes are mostly colloids of more or less slight solubility, *e.g.*, benzopurpurin. The direct cotton colours were supposed to exist in the colloidal condition to a much greater extent than the dyes of the acid and basic groups, and this would explain them being taken up direct by the cotton fibre. Wool and silk enter into combination with dyes, forming membranous colloidal salts; leather in tanning forms a similar surface. Hence his theory is that the dyer 'imitates Nature' in 'forming a protective insoluble colloid membrane on the outside of the fibre.' Biltz[49] also showed that colloidal solutions of inorganic substances like selenium, tellurium, gold or molybdenum blue would dye wool or silk, and that analogously with organic dyestuffs an electrolyte (salt) hastened, while a protective colloid retarded, the process.

Later research has confirmed much of Krafft's work, if it has also served to point out his errors, most glaring of which is of course that of the 'protective exterior membrane.' Certainly the adsorption process is by its very nature largely confined to the surfaces, but the entire structure of a sol (or gel) may be permeated by another substance, colloid or crystalloid, and then, according to McBain and Zsigmondy, the term 'sorption' is more descriptive of the phenomenon. Sisley takes exception to the use of the word 'adsorption' which is now largely used in colloid chemistry to indicate the extraction of a dissolved body by a solid. He submits that the word is no improvement on absorption and that so-called adsorption compounds are in no way distinguishable from chemical

[47] 1896-9, *Berichte*, 27, 28, 29, 30, 32.
[48] Zsigmondy, p. 67, 157 *et seq.*
[49] *Journ. Soc. Dyers and Col.* 1904, p. 145; 1905, p. 276.

compounds. It is probable that their formation is incomplete, and this would explain their not obeying the law of multiple proportions.

Other workers besides Krafft and Biltz are of the opinion that many dyestuffs form colloidal solutions. Teague,[50] Buxton, and Vignon base their conclusions with Krafft on diffusion experiments, Pelet-Jolivet[51] and Wild on their ultramicroscopic studies. Knecht and Batey[52] and later Donnan and Harris[53] deny the colloidal nature of benzopurpurine, chrysophenine, and Congo red on grounds that their electrical conductivities are normal and that they exert osmotic pressure. The work of Donnan and Harris is important and leads to the view that measurements of the osmotic pressure are of no value unless account be taken of the presence of an electrolyte (if present). The electrolyte distributes itself unequally on the two sides of the dialysing membrane and sets up an opposing osmotic pressure. Zsigmondy, considering their experiments, also those of Bayliss,[54] Teague and Buxton,[55] Rachlmann v. Vegesack,[56] Biltz and Bredig, places Congo red and all the other azo- dyestuffs of its class among the colloids, owing to their low diffusibility and optical visibility (in the ultramicroscope). On boiling Congo red dissociates; it is extremely sensitive to the presence of carbon dioxide in diffusing, but in the matter of conductivity and osmotic stress it behaves like a crystalloid or electrolyte; the conclusion being that the salt is dissolved as molecules, but the presence of extremely minute amounts of electrolytes causes aggregation into submicrons. Dyestuffs with the alizarin group are highly colloidal, while the dyestuffs containing sulphonic groups not only form very soluble compounds in water, but their salts are very dialysable even with molecules of from 76–78 atoms, yet, according to Biltz,[57] molecules of from 70 to 95 atoms should not diffuse.

In the light of these facts, all the recent research into the properties of colloids has its direct bearing upon the theory of dyeing.

Following upon Krafft, P. D. Zacharias published in 1900 a 'Farbentheorie,' of which the German translation appeared in 1908. His theory meanwhile developed in a series of essays in the 'Farbenzeitung,' 1901, **12**, 149 and 165, and 'Ber. d.d. chem. Ges.' 1905. His earlier theory is one of colloid interdiffusion plus adhesion. He discounts the chemical theory altogether, objects to the solid solution theory pure and simple, but, recognising the colloidal nature of the dyes and of the fibres, he suggests an interdiffusion plus precipitation, followed by or resulting in an adhesion, whose nature he does not particularise. His later theory, which he insists does not essentially vary from his first statements, follows upon the researches of Graham, Krafft, Justin-Mueller, Biltz and Zsigmondy (Biltz and Zacharias variously quarrelled about the originality of each other's theory and experiments; while Zacharias continuously and pugnaciously defends his theory, it is Biltz who brought forward the experimental material for such a theory—no such experimental data

[50] *Zeitschr. für Phys. Chem.* 1907, **60**, p. 419.
[51] *Zeitschr. Chem. Ind. Koll.* 1908, **3**, 174.
[52] *Journ. Soc. Dyers and Col.* 1909, **25**, 194.
[53] *Chem. Soc. Trans.* 1911, **99**, 1554.
[54] *Proc. Roy. Soc.* 1909, **81B**, 269.
[55] *loc. cit.*
[56] *Zeitschr. physikal. Chem.* 1910, **73**, 481.
[57] *Ibid.*, 1911, **77**, 91; also *Gedankboek*, van Bemmelen, 1910, 108.

having been furnished by Zacharias). He now places the dyeing process in close relation to that of solution, with its phenomena of hydrolysis and ionisation, on the border-line between chemistry and physics. The cohesion between fibre and dye he now conceives to be possibly electrical in character, comparable to the combination of ions. Essentially, dyeing is the coagulation of a colloid in or upon another colloid, in such a form as to be insoluble; the electrolyte present in the bath causes such coagulation by its electrical effects on the colloid solute and its solvent He does not now deny the possibility of subsequent chemical combination between the cohering fibre and dye, particularly in the case of animal fibres.

W. P. Dreaper also did something to bring the observed dyeing phenomena into line with the evolving colloid theory. In his earlier papers his theory is one of endosmosis, proportional to pressure and to the absolute temperature, coupled with chemical combination; he also inclines to the solid solution theory, applying Linder and Picton's idea of 'pseudo-solution' to the phenomena of dyeing. Finally he rejects both the chemical and the solid solution theories, upholding one of pure adsorption by the fibre, acting as a more or less dry gel, of the hydrosols of the various dyes. Dyeing is always carried on in the wet condition, so that the fibre may be sufficiently hydrated to act as a hydrogel of the gelatine type; the state of hydration Dreaper finds to influence the amount of any solution adsorbed. His text book (1906) 'Chemistry and Physics of Dyeing' gives a very broad and somewhat indecisive theory of 'the phenomena which take place in dyeing,' including: (1) 'A solution state of the dye, within certain limits of aggregation, determined by the laws of size'; (2) 'a fibre state corresponding to this state of aggregation, and of a permeable nature'; (3) 'effective localisation of the dye within the fibre area, due to surface concentration phenomena'; (4) 'localisation of salts, acids, &c., within the fibre area'; (5) 'indirect entrance of dye aggregate by molecular migration with subsequent re-formation of aggregates within the fibre area, according to the laws of size'; (6) 'de-solution, due to secondary attraction between the fibre substance and the dye, or by reduced surface energy phenomena, or concentration effects'; (7) 'in some cases, primary or chemical action may play some part at this stage; this may even, in some cases, take the place of de-solution phenomena'; (8) 'dissociation effects in the case of basic dyes which may lead to the production of very basic salts in a high state of aggregation within the fibre area.' He is aware of the electro-positive or electro-negative nature of all colloids, but does not connect this with the coagulating (he calls it 'degrading') influence of crystalloids in the dissolved colloid.

A similar cognition of the diverse and seemingly irreconcilable nature of the dyeing processes was published by Grehm and Rotheli,[58] who, after an exhaustive criticism of all existing theories and evidence, conclude that each existent theory can find place in the final and adequate one. They were the first to show that cotton takes up direct cotton colours in an unchanged condition. Later Gnehm and Käufler performed the following experiment: a skein of cotton dyed with benzopurpurin was boiled with two undyed skeins in a small beaker. After drying, all three skeins were alike. This observation is in direct opposition to Krafft's

[58] *Zeitschr. f. angewandte Chemie*, 1898, pp. 482, 501.

theory of colloidal precipitation, for if the colour in the dyed skein is due to the formation of a colloid precipitate, it cannot be conceived that in one case solution should ensue and in another precipitation.

Wilhelm Ostwald,[59] M. van Bemmelen,[60] H. Freundlich,[61] G. Losev,[62] L. Pelet-Jolivet,[63] and W. Biltz [64] investigated the laws governing adsorptions by solids such as charcoal, of crystalloids and colloids, and the dyeing of mineral substances by dyestuffs. The associated phenomena of contact-electrification were also studied by Perrin,[65] who formulated laws,[66] and by Pelet-Jolivet and Grand,[67] Miolati,[68] Gee and Harrison,[69] and Knecht.[70] Further work in the same fields—by Svante Arrhenius [71] (diffusion of hydrosols and adsorption isotherms), O. Bütschli [72] (structure of gels, and influence of hydration on a dried gel), Wolfgang Ostwald [73] (classification of disperse systems, conductivity of metal hydrosols, electrical coagulation of suspensions, &c.), A. Lottermoser [74] (metallic hydrosols, solid sols, freezing of metallic hydrosols, mutual precipitation), W. Pauli [75] (electric charge and coagulation of albumen, precipitation by electrolytes, internal friction of albuminous sols, structure of jellies, turgescence of the same and conditions governing its rapidity), P. P. von Weimarn[76] (emulsoids and suspensoids, the formation of jellies from crystalloid solutions and the crystallisation of colloids, laws governing surface tension in two-phase systems), Emil Hatschek [77] and Zsigmondy,[78] working with Siedentopf, Ambronn, Heyer, Kirchner, Schultz and Wilke Dorfurt—has resulted in a comprehensive theory of colloidal systems, which many of the investigators have themselves applied to the dyeing process.

The idea of 'solution' is to be widened to embrace all possible combinations of a solid, liquid or gaseous disperse phase with a solid, liquid or gaseous continuous phase.[79] The most common solutions still are those having a liquid continuous phase, and the most common solvent is water—few, if any, substances refusing to go into colloid, if not crystalloidal, solution in water. Now, the obvious method of differentiating between crystalloids and colloids is by means of dialysis, whether it be carried out by the Graham dialyser or the far more complicated and efficient ones of Kühne, Jordis, or Zsigmondy and Heyer. But a substance may be colloid in some solvents and crystalloid in others; nor is it only crystal-

[59] *Zeitschr. f. phys. Chemie*, 1890, **6**, 71–82; *Lehrbuch der allgem. Chemie*, 1 Aufl. **1**, 778–791 (1885), 2 Aufl. **2**, **3**, 217 *et seq.* (1906).

[60] *Zeitschr. f. anorg. Chemie*, 1903, **23**, 238, **18**, 114–7, **13**, 350.

[61] 'Kapillar Chemie,' 1909, *Zeitschr. f. phys. Chemie*, 1909, **44**, 129.

[62] *Zeitschr. f. phys. Chemie*, 1907, **59**, 284–312, &c.

[63] 'Theorie des Farbeprozesses' (1910), *Kolloidzeitschr.* 1909, **5**, 238–243.

[64] *Berichte*, 1904, **37**, 1095–1116; van Bemmelen, *Gedankboek*, 1910, 108–20.

[65] *Annales de Chim.* 1909, **18**, 5–114; *Comptes Rendus*, 1903, **136**, 1388–1391, **137**, 513, 564.

[66] *Journal de Chim. Physique*, 1904, p. 619, and 1905, p. 100.

[67] *Rev. Gen.* 1907, p. 225; *Koll. Zeitschr.* 1907, **2**, 41.

[68] *Berichte*, 1893, **26**, 1788.

[69] 'The electrical theory of dyeing,' 1910, *Journ. Soc. Dyers and Col.* 1911, p. 279.

[70] *Journ. Soc. Dyers and Col.* 1909, **25**, No. 7.

[71] *Immuno Chemie*, 1907, p. 17.

[72-73] See Zsigmondy, *Kolloid Chemie.*

[74] 'Zur Lehre von den Zustanden der Materie' in *Koll. Zeitschr.* 1907–9, 2–5. 'Grundzuge der Dispersoid Chemie' (1911), *Chemikerzeitung*, p. 725.

[77] *Introduction to the Physics and Chemistry of Colloids*, 1916.

[78] *Kolloid Chemie*, 1912.

[79] Zsigmondy, *ibid.* p. 25.

loids that form geometric crystals; colloid gold, silver, albumen, globulin and hæmoglobin will all give crystals, while it is possible to obtain 'globomorphous' sodium chloride, and many crystalloid solutions pass through a jelly-like stage immediately before solidifying into crystals. It is more correct to speak of a 'colloidal state of matter' than of 'colloids' as a sharply defined class. Colloidal solutions are either 'suspensoid' (*i.e.*, having a solid disperse phase) or 'emulsoid' (having a finely divided liquid disperse phase); the particles or 'micelli' varying in size from ·1 $\mu\mu$ (crystalloid) to 1 $\mu\mu$ (hydrosols) to 100 $\mu\mu$ (turbidities) and from 100 $\mu\mu$ to 1 mm. (suspensions fine or coarse). Below 1000 $\mu\mu$ the so-called Brownian movement is visible, both in true colloid-solutions and fine suspensions; the motion is the more rapid the smaller the particles are; it does not vary on admitting or excluding the dark heat-rays; it is independent of the direction of admitted light-rays, or the length and intensity of its subjection to these; it will continue for months and even years; it does not depend on the charge upon the particles; it is affected by dilution, and the particles appear to influence one another. Various theories have been put forward to explain it. Quincke[80] considered it due to the spreading of liquid layers over the surfaces of the particles; Wiener,[81] Cantori, Renard, Boussinesq, and Gourg based it upon collisions between the particles and the molecules of the solvent; Einstein,[82] von Smoluchowski,[83] Zsigmondy,[84] The. Svedberg,[85] and Perrin[86] ascribe it to kinetic energy.

The particles migrate, under the influence of the electric current ('cataphoresis'), in a direction determined by their charge. The same colloidal solution may be positive or negative—it depends on the nature of the continuous phase ('intermicellary liquid') and the electrolytes it may contain. The direction can be measured by Coehn's[87] apparatus, or that of A. Cotton and H. Mouton,[88] or of The. Svedberg[89]; colloidal iron oxide, cadmium hydroxide, titanic acid, &c., and all basic dyestuffs, colloid or crystalloid, are positive and wander to the cathode; colloidal gold, silver, platinum, sulphides, mastic, starch, gums, stannic acid, molybdenum blue, &c., and all acid dyestuffs, colloid or crystalloid, are negative and wander to the anode.[90] A trace of added alkali causes a neutral colloid (*e.g.*, suspended white of egg in pure water) to become negative, added acid causes a cathodic convection.[91] The electrical

[80] *Verh. d. Ges. d. Naturf. u. Arzte*, 1898; *Beibl. zu d. Annalen d. Phys.* 1899, **23**, 934–7.

[81] *Poggendorff's Annalen d. Phys. u. Chemie*, 1863, 118, 79–94.

[82] *Drude's Annalen d. Phys.* (4) 1905, **17**, 549–560; 1906, **19**, 371–381; *Zeitschr. f. Elektrochemie*, 1908, **14**, 235–239.

[83] *Drude's Annalen d. Phys.* (4) 1906, **21**, 756–780; 1908, **25**, 205–226.

[84] *Zeitschr. f. Elektrochemie*, 1902, **8**, 684–687; *Koll. Chemie*, p. 38–9; *Zur Erkenntnis der Kolloide*, 1905, S. 106–111, with tables.

[85] 'Studien zur Lehre von den kolloiden Lösungen,' 1907, 125–160; *Zeitschr. f. phys. Chem.* 1910, **73**, 547–556.

[86] *Annales de Chimie et de Phys.* 1909, (8) **18**, 5–114.

[87] *Zeitschr. f. Elektrochemie*, 1909, **15**, 653.

[88] *Les Ultramicroscopes*, &c., 1906, p. 144.

[89] *Loc. cit.*

[90] Zsigmondy, *Kolloid Chemie*, p. 44.

[91] Hardy, *Journal of Physiology*, 1899, **24**, 288–304; Hardy, *Zeitschr. f. p. Chemie*, 1900, **33**, 385–400; Perrin, *Comptes Rendus*, 1903, **136**, 1388–1391; 1903, **137**, 513–514, 564–6.

property of electrolytes is well known to be due to their dissociation into negative anions and positive cations ; the charge on the colloid particles is not so easy to explain, as they are not generally supposed to be ionised. Yet Zsigmondy gives three various explanations,[92] and Bredig [93] and Billitzer [94] assume the same, *i.e.*, difference of dielectric constant between particle and intermicellary fluid ; capture (*e.g.*, colloid gold with H ions) or deposition of ions. Hardy [95] has the distinction of pointing out that it is the electrification of the particles of any irreversible colloid that causes it to remain in solution ; if an electrolyte of opposite charge be added till the isoelectric point be reached, the colloid will coagulate into a gel ; the ions of the electrolyte bearing the opposite charge to the colloid particles also take part in the precipitation.[96] Schulze [97] has pointed out, and this has been many times corroborated, that the valency of the ion is of great influence in this coagulating process : a trivalent ion is worth 1,000 monovalent or 30 divalent ions. The curve is the same as the adsorptions curve, as Freundlich [98] has pointed out, and Pelet-Jolivet's [99] table of comparisons between the laws of contact electrification, colloid coagulation, dyeing and capillary attraction bears out in a remarkable way. Not only do crystalloids precipitate colloids, but two colloids of opposite charge will precipitate each other, unless one is in overwhelming excess of the other ; there is a more or less wide zone within which mutual coagulation will take place, though there is only one point at which the charges actually neutralise each other. For dyeing, this rule is of the widest importance.[100]

If the dry gel of a reversible colloid like gelatine or agar be put into water to be dissolved, it behaves in a manner quite distinct from a crystalloid. The latter gives off particles from its surface till all is dissolved, in a manner analogous to the evaporation or sublimation in a gaseous medium, and the solution obeys Boyle-Gay-Lussac's laws of gases, within certain limits. The gelatine swells up and absorbs the water into its own substance, but does not dissolve until the temperature rises to above 25° C.

Van Bemmelen and Batschli believed that jellies possessed a porous structure of microscopic dimensions, but this theory is now abandoned ; such pores can be produced by irregular contraction under the action of alcohol or chromic acid, and the structure of natural jellies is molecular, and they are of the nature of solid solutions. Capillarity may cause imbibition but cannot produce swelling in itself, though it may liberate the elasticity of the imbibing substance, as water does that of a dried sponge.

Similar phenomena will explain the adsorption of liquids by charcoal, unglazed pottery, &c., though, as von Georgievics points out, not the decolorisation of liquids : this is, according to Knecht and Suida,[101] due to the activity of the nitrogen compounds of the charcoal, and to the acid nature of the silicates.

[92] *Kolloid Chemie*, p. 48.
[93] *Anorganische Fermente*, 1901, p. 16.
[94] *Zeitschr. f. Elektrochemie*, 1902, **8**, 638–642 ; *Zeitschr. f. phys. Chemie*, 1903, **45**, 307–330.
[95] *Loc. cit.*
[96] See also Dreaper, *Chemistry and Physics of Dyeing*, p. 123.
[97] *Journ. f. praktische Chemie*, 1882 (2), 25, 431–452 ; 1883, **27**, 320–332.
[98] *Zeitschr. für phys. Chemie*, 1910, **73**, pp. 385–423.
[99] *Theorie des Farbeprozesses*, 1910.
[100] See Zsigmondy, *Koll. Chem.*, Ch. 98, 'Kolloidfallung der Farbstoffe.'
[101] *Sitzungsber. d. Akad. d. Wiss.*, Wien, 1904, 113, 11b, 725–761.

Pieces of such colourless and transparent silicic-acid-gel thrown into colloidal dye solutions Zsigmondy found to behave as 'ultra-filters,' the dispersion-medium being absorbed as by a sponge, and the dye-particles held on the surface of the gel-particles in a semiliquid state. Silk, cotton, and wool fibres show a similar hygroscopy and were described by Dreaper. as 'colloidal substances dry to the touch,' like solid gelatine. Like it, they swell up in water and other solvents but do not dissolve; they may be looked on as irreversible gels, like silicic acid. Their 'pores,' however, are not of the extreme minuteness of those of the latter substance: they do not show anything like the same optical homogeneity; and therefore they are not 'ultra-filters' to the same degree. Moreover, the fact that they show no readiness to enter into solution, in spite of their 'swelling,' causes Justin-Mueller [102] to suggest the name 'turgoids,' not 'colloids,' for them, and to call the process turgescence and not colloidal solution. He considers this turgescence of the fibre to be a necessary part of the process of adsorption of the dye; colours that rub off do so because adhesion, not adsorption, has taken place, and the dye has been 'salted out' or coagulated on the fibre. Both the deposition and the adsorption are reversible according as the adsorption-coefficient and solubility-cofficient approach each other.

Some such laws appear to be followed as were noticed by Pelet-Jolivet and his assistants in recording the capillary attraction of filter-paper on various kinds of solutions: the height to which the coloured layer, or the layer that gives a direct reaction acid or basic, appeared to rise, was found to agree in a remarkable way with the observed electrical and colloid-precipitating effects of the same solutions. Schoenbein, W. Ostbald, Goppelsroder, and Fichter and Sahlbom have recorded the following results: Alkali and acid solutions give reaction up to seven-tenths of the wetted paper; calcium carbonate only about one-tenth, and barium hydrate about three-tenths. Positively-charged colloids are found to be deposited on the paper at the surface of the liquid, while negative colloids mount with the water. (Thus Fichter and Sahlbom refer to the currents set up in the capillaries of the paper: even in glass capillaries water rises much higher than basic dyestuff solutions or positive colloids in general.) Thus any influence which causes colloidal coagulation, or decreases solubility, limits the capillary rise and favours dyeing; the influences which keep the particles small and disperse act in the other direction and are against rapidity of colouring. From this the actual value of 'assistants' in the dye-bath may be deduced, without postulating a liberation of the free dye-acid, which has been diversely shown to be little, if any, more effective pure than combined to form a dye salt.

The work of Alexander [103] is of interest as showing the influence of protective colloids on dye solutions. He has previously pointed out that, after the addition of protective colloids (gelatine &c.) to solutions of benzopurpurin, dilute acids produce colour changes analogous to those adsorbed in the dyed animal fibres. In the case of a dilute solution of benzopurpurin, addition of dilute mineral acid quickly changes the bright red colour to dark blue, and stronger acid coagulates the dye which settles out of solution. If gelatine is added to the benzopurpurin solution, dilute mineral acids give a claret-red solution, and stronger

[102] *Chemikerzeitung*, p. 845, 1914.
[103] *Journ. Soc. Chem. Ind.* 1911, p. 517.

acid changes the shade to chocolate-brown, without, however, causing any precipitate. Alexander has examined these colour-changes at the ordinary temperature in the ultra-microscope, and reports—dilute benzopurpurin solution shows a field full of ultra-microns which from their brilliancy and motion appear to be 50–60$\mu\mu$ in size. When a little acid is added, the ultra-microns gradually gather together into clumps, or groups, whose motion decreases as their size increases, until the whole of the dye is deposited in coagulated masses of bright ultra-microns. Stronger acid causes instant coagulation in large masses when acid is added to the gelatine dye solution; no change is produced unless the acid is strong enough to cause a more or less extensive agglutination of ultra-microns into small groups of 2 or 3, which, however, have still sufficient motion to keep afloat. The cause of the variation in the colour-changes produced by immersion in dilute acid on the different fibres dyed with benzopurpurin is due (according to author) to their difference in protecting action on the adsorbed dye. A practical application for the use of protective colloids is found in Feilmann's English patent, 10,693, 1906, where the employment of casein is made to produce colloidal solutions of various unsulphonated dyestuffs, particularly azo- dyes. But this application has not found much use up to the present.

Similarly Mohlau and Zimmermann[104] produce colloidal indigo by means of protalbumic and lysalbumic acids—also Fabrik v. Heyden produce the same substance by the use of various protein substances.[105]

The phenomenon of 'contact electrification' and its value in dyeing remains. Whenever two substances solid, liquid, or gaseous are in contact, having a common surface, all kinds of forces come into play, which are difficult indeed to study when acting between solid and solid or solid and liquid or solid and gas, but between liquid and gas have been formulated. Surface tension and surface electrification are the problems which particularly concern colloidalists, the surfaces between the disperse and the continuous phase being so immense in comparison with the mass.

Gibbs[106] enunciated the theorem 'Those substances which lower the surface tension of a solution with respect to another phase must concentrate themselves upon the latter.' This can be experimentally proved with gas-liquid and liquid-liquid systems, for it is possible to measure their surface tensions; but Freundlich has lately shown that those substances which lower the surface tension between two liquids are strongly adsorbed, not only by these but also by solid bodies; hence the rule would seem to have general application. Moreover, the adsorption-isotherm (showing quantitative adsorption by solid bodies) will hold also for the gas-liquid and liquid-liquid boundary. Freundlich, Schmidt[107] and Svante Arrhenius[108] have given formulae for this adsorption, which within certain limits holds for the adsorption of crystalloids by charcoal and by hydrogels.[109] Ultra-microns of one colloid likewise adsorb ultra-microns of another colloid, and even when they both bear the same charge; this can be seen in the ultra-microscope and goes

[104] *Zeitschr. f. Farben und Textil Chemie*, 1903, 25.
[105] German Patent Application, 112,051, 1903.
[106] *Thermo-Dynamische Studien*, p. 321.
[107] *Zeitschr. f. phys. Chem.* 1911, **77**, 641–660; 1912, **78**, 667–681.
[108] *Meddelanden från K. Vetenskapsakad. Nobelinstitut*, 1911, 2 N. 7.
[109] *Van Bemmelen.*

to show that the electrolyte-coagulation theory is not quite adequate to explain all dyeing phenomena. When one colloid so unites with the other it forms a 'protective colloid' and shows the utmost reluctance to coagulate. This is connected with P. P. von Weimarn's 'Grundgesetz der Dispersoidologie' : 'When a substance suffers physical or chemical division it strives with all possible means for a diminution of its free surface energy.' This diminution of surface energy may take place by coagulation, which, however, is impossible so long as all the particles have the same charge, and only takes place in presence of an electrolyte or under influence of a current or by deposition upon a surface whose charge is opposite to their own, giving adsorption according to Freundlich's rules. Perrin's[110] and Pelet-Jolivet's researches into the contact charges which appear on various solid substances, including textile fibres, when brought into contact with liquids show, not only a definite 'latent heat of adsorption,' but also a charge (measured by the electrosmosis of the liquid through the diaphragm) in the case of ionising solvents, but not of non-ionising solvents like chloroform, petroleum, and benzol. All solid substances take on a positive charge in an acid liquid, a negative charge in an alkaline liquid; the difference of potential is greater when the number of H ions is greater, and smaller in presence of a greater number of OH ions. These phenomena show a remarkable parallelism to the results observed in the coagulation of colloids and point to some deep-seated analogy. Wool, cotton, silk, &c., follow the general charge-law in acids and alkalies, but they all take a negative charge already in pure distilled water; this charge is increased in contact with alkaline solutions and decreased in acid solutions with silk and wool it is possible to show an actual change in sign of charge.

The work of Linder and Picton[111] may be mentioned here. They stated that dyeing is connected with the electrical charges which substances carry when existing in colloidal solution. They experimented on colloidal ferric hydroxide and basic dyes which carry positive charges and arsenious sulphide and acid dyes which are negatively charged. Hence—as two oppositely-charged colloidal solutions precipitate one another—soluble blue (acid) precipitates ferric hydroxide, but methyl violet does not. Exactly the reverse process occurs with arsenious sulphide. Ammonium sulphate also precipitates colloidal ferric hydroxide, but they found a distinction between its action and that of the dye. A definite quantity only of the salt is required to precipitate the colloid, and more added remains in solution. However, with the dye, after the colloid had been precipitated the dye continued to be adsorbed by the ferric hydroxide as a whole. They explained this by assuming that the precipitated colloid still retained a portion of its original charge, and that by virtue of this it still continued to take up more dye. The same kind of action was supposed to take place in dyeing—the fibre taking the place of ferric hydroxide or arsenious sulphide.

These facts will account for the phenomena of dyeing wool with a basic dyestuff of the methylene-blue type: it is an evident case of mutual discharge and consequent precipitation by two oppositely-charged colloids,

[110] *Loc. cit.*

[111] *Journ. Chem. Soc.* 1905, pp. 1931-1935. See also *Journ. Chem. Soc.* 1892, **61**, 114, 137, 148; *ibid.*, 1895, **67**, 63; *ibid.*, 1897, **71**, 568.

and the effect of adding either acid, base, or salt to the bath can also be demonstrated. But the colloid-precipitation theory can by no means be directly applied to dyeing with acid dyes upon animal fibres in the neutral bath: the fibre charges itself negatively, the dye also has a negative charge, and no two colloids of the same sign will precipitate each other. This leads Pelet-Jolivet[112] to revert to the adsorption theory, assuming that the dyestuffs act as unhydrolysed electrolytes in their solutions, and are adsorbed according to the valency of their combining ion, *e.g.*—the sodium salt of the colour acid should dye less strongly than the calcium or magnesium salt, and this less strongly than the aluminium salt or than the free acid with its hydrogen ion; similarly the hydrochloride of a basic dyestuff should give weaker colours than the sulphate or than the phosphate, or finally than the hydrate with its OH ion. This theory Pelet was able to demonstrate clearly by experiments both with acid and basic dyes upon wool; he concludes that the dyes, as von Georgievics, Walker Appleyard, and Vignon had already stated, act as dissociable electrolytes in the bath and dye according to valency—the H and OH ions always having disproportionate action to their valency.

These results also accord with his experiments (following Goppelsroder[113]) in capillary-ascent of various dyes (in water-solution) in strips of linen, cotton, flannel, and silk cloth, as well as filter-paper. Positive dyestuffs (colloid) cease to ascend at the actual surface of the liquid; added acids cause them to ascend, and decrease the ascent of acid dyes; alkalies will not cause acid dyes to ascend further, and actually decrease the ascent of basic dyes.

The dyeing process by adsorption plus dissociation Pelet ingeniously explains by assuming an accompanying dissociation of the water; the fibre becomes covered in the case of basic dyes by a 'double layer' of H and OH ions, which, like those of the sodium, &c., base in acid dyes and the SO_4, &c., ion in basic dyes, are very small and mobile in contrast with the large organic ion, and therefore reach the fibre first and deposit themselves as a film upon it, giving it thus their charge. The organic ion of the dyestuff has an opposite charge to these, and fixes itself, by a process analogous to coagulation, upon them. The actual existence of this 'double layer,' which by selection results in a fixation of the dye accompanied by a quantitative survival of the acid in the bath, has been demonstrated by Pelet, von Helmholtz, G. Quincke, and A. Pellot to exist on the surface of solid bodies immersed in water. Similar cases of chemical action subsequent to adsorption have been noticed by H. Freundlich and W. Neumann.[114]

It would appear that in this theory—which takes account of the electrical properties of solutions colloidal and crystalloidal, of the phenomena of contact-electrification and surface-tension expressed in terms of capillary attraction, of the effect of temperature upon all these, without denying the possibility of chemical reaction between the fibre and the dye presented to it—lines are laid down upon which an adequate theory of the dyeing process may develop.

[112] *Theorie des Farbeprozesses*, p. 105, Pelet-Jolivet and N. Anderson, *Koll. Zeitschr.* 1908, **3**, 206.

[113] 'Verhandlungen der Naturforschenden Gesellschaft zu Basel,' *Koll. Zeitschr.* 1909–10, **4**, 5, 6.

[114] *Zeitschr. f. phys. Chem.* **67**, 538.

Wm. Harrison and Haldane Gee [115] proceeded now to carry out their experiments testing this electrical theory and found it to explain phenomena observed better than the adsorption theory, which Lewis [116] had discredited on the grounds that it demands a decrease in amount of dye adsorbed under increase of temperature. These authors claim that it is always an electrical phenomenon: if the dye be colloid, then coagulation results from neutralisation of charge; if not colloidal, then it is ionised in solution and deposited by contact-electrification charges acting on the ions.

They discovered a most important phenomenon, *i.e.*, that the maximum negative charge attained by wool, silk, and cotton was at 40°. This is undoubtedly strong evidence in favour of an electrical phenomenon, as Brown [117] found that wool absorbed most basic colour at about 40°.

Harrison refers to the physical constitution of the fibres, as the surface (on which the charge rests and to which the dye-particles wander to fix themselves) is greatly increased by the porosity and irregularity of the fibre. He suggests that the dye-particles, if very large, will not fix on silk so well as on wool or as on cotton (this being the order of increasing size of their pores); by this theory Harrison also explains the adsorption and fixation of the direct cotton-colours.

In his dyeing experiments various salts, &c., are added, none of which tend to retard coagulation or to decrease the size of the particles, but rather the reverse. The dye should, therefore, be fastest dyed without salts, and this Harrison finds to be the case. Also, as an increase in temperature decreases the size of the particles, it should increase the fastness of the resulting dyeings. This also he finds to be true.

Feilmann expressed his ideas of dyeing similarly to those of Gee and Harrison, *i.e.*, that the dye was attracted electrically by the oppositely-charged fibre. He also asserted that the ion of the dyestuff penetrated the fibre more or less deeply, and was retained either because the fibre acted as a protective colloid or because chemical action took place between the ion and the fibre.

COLLOID CHEMISTRY IN THE FERMENTATION INDUSTRIES.

By Prof. ADRIAN J. BROWN, *University of Birmingham.*

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'The Diastatic Coagulation of Starch.' A. FERNBACH and J. WOLFF. ('Comp. Rend.' 1904, **139**, 217. Abst. 'J. Inst. Brewing,' 1905, **11**, 190.)

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[115] *Trans. Faraday Society*, 1910, April (*Journ. Munic. Sch. Techn. Manchester*, vol. iv., 1911, pp. 131–154), Paper (Harrison) *Journ. Soc. Dyers and Col.*, 1911, p. 279. They append to their paper a translation of Pelet's tables of affinity between colloid-coagulation, contact-electrification, capillary ascent and dyeing, as does also Zsigmondy (*Kolloid Chemie*, p. 229).

[116] *Phil. Mag.* 1908 (6) **15**, p. 499.

[117] *Journ. Soc. Dyers and Col.* 1901, p. 92.

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'The Selective Permeability of the Coverings of the Seeds of *Hordeum vulgare*.' ADRIAN J. BROWN. ('Proc. Royal Soc. **B.** Vol. **81**, 1909,)

The seeds are furnished with a covering permeable by water and certain classes of solutes when in aqueous solution; with the majority of solutes, however, the covering behaves as a true semipermeable membrane.

'Colloidal State of Brewing Materials, and its Importance for the Brewery.' C. J. LINTNER. ('Zeitschr. ges. Brauw.' 1909, **32**, 633. Abst. 'J. Inst. Brewing, 1910, **16**, 211.)

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'Adsorption of various Substances by Starches,' H. LLOYD. ('J. Amer. Chem. Soc.' 1911, **33**, 1213. Abst. 'J. Inst. Brewing,' 1911, **17**, 693.)

'Cause of Precipitation in Finished Pasteurised Bottled Beer.' F. EMSLANDER. ('J. Inst. Brewing,' 1912, **18**, 484.)

The 'head-retaining power' and 'palatefulness' of beer are due to ultramicroscopic particles of albumen existing in the form of an emulsion-colloid. Turbidity is occasioned by coagulation of the particles induced by physical or chemical influences. The stabilising influence of acids (*i.e.*, H ions) is discussed.

L. WALLERSTEIN. New York. (Eng. Patent 12,350, May 22, 1911.)

Object of process is the rendering of beer chill-proof by treatment previous to bottling with proteolytic enzymes (*e.g.*, pepsin or papain), to hydrolyse albumins causing turbidity. (See 'J. Inst. Brewing,' 1912, **18**, 491.)

'Colloidal Chemistry and Brewing.' EMIL HATSCHEK ('J. Inst. Brewing,' 1912, **18**, 494.)

A general survey of colloidal chemistry, with special reference to questions such as 'head' formation, haze, &c., which are of particular importance in brewing.

'Plant Colloids: Gelatinisation of Starch in Presence of Crystalloids.' M. SAMEC. ('Kolloidchem. Beiheft,' 1911, **3**, 123. Abst. 'J. Inst. Brewing,' 1912, **18**, 694.)

Discusses the influence of crystalloids on temperature of gelatinisation.

'Reactions of Tannin and their Importance in Brewing.' A. REICHARD. ('Zeitschr. Chem. und Ind. Kolloide,' 1912, 209. Abst. 'J. Inst. Brewing,' 1912, **18**, 695.)

'The Tannin in the Testa of the Barleycorn.' A. REICHARD. ('Zeitschr. Chem. u. Ind. Kolloide,' 1912, 214. Abst. 'J. Inst. Brewing,' 1912, **18**, 696.)

Author suggests that the selective permeability of the inner covering of barleycorn may be occasioned by the tannin present. (See A. J. BROWN, p. 1.)

'Beer Haze.' F. SCHÖNFELD. ('Wochenschr. Brau.' 1912, 29, 557. Abst. 'J. Inst. Brewing,' 1912, **18**, 696.)

The paper contains illustrations of different types of beer haze.

'The Influence of Temperature on the Absorption of Water by the Seeds of *Hordeum vulgare* in relation to the Temperature Coefficient of Chemical Change.' ADRIAN J. BROWN and F. P. WORLEY. ('Proc. of Royal Soc.' **B.** 1912, **85**, 546.)

The velocity with which water is adsorbed by the seeds is an exponential function of the temperature, and is comparable with the vapour pressure of water, which is also approximately an exponential function of the temperature. The velocity of adsorption of water from a solution of ethyl acetate is also an exponential function of the temperature, but the actual velocity is higher in the presence of ethyl acetate than in the presence of pure water. Probably the partial pressure of water vapour is increased by the presence of ethyl acetate.

'Use of Gelatinous Silica for the Clarification of Beer.' P. Deprax. ('Ann. Brass. et Dist.' 1912, 15, 410. Abst. 'J. Inst. Brewing,' 1913, 19, 52.)

'On the Flocculation or "Break" of Worts and Beers and its Significance in Brewing Practice.' Horace T. Brown. ('J. Inst. Brewing,' 1913, 19, 84.)

The persistent turbidity produced on cooling a hopped malt wort is occasioned by a suspension of particles of a tannin-protein compound soluble in hot wort, insoluble in cold. Most of the particles are formed during cooling between the limits of 49° C. and 27° C. If the wort is strongly agitated when cooling between these limits, flocculation takes place, otherwise flocculation is rendered difficult owing to the protective influence of the dextrins of the wort. A suspension of the tannin-protein compound is injurious to the propagation and fermentative power of yeast, and adversely affects the flavour of the resulting beer owing to adsorption of hop resin on the surface of the suspended particles. A technical means of inducing flocculation during cooling of the wort is indicated.

'Practical Observations and Studies of Albumin Turbidities in Beer caused by Tin and Iron.' G. L. Goob. ('Eighth Internat. Cong. Appl. Chemistry,' 1912. Abst. 'J. Inst. Brewing,' 1913, 19, 147.)

'Head on Beer.' A. Fernbach. ('Ann. Brass. et Dist.' 1913, 16, 145. Abst. 'J. Inst. Brewing,' 1913, 19, 400.)

The relation of the colloids of beer to the formation, nature, and retention of 'head' is discussed.

'Electrical Dialysis of Enzymes: Application of the Principle to the Purification of Malt Diastase.' M. Lisbonne and M. Vulquin. ('Journ. de Physiol. et Pathol.' 1913, 15, 24. Abst. 'J. Inst. Brewing,' 1914, 20, 64.)

'Removal of Oil from Condenser Water by Electrolysis.' H. Winkelmann. ('Zeitschr. ges. Brauw. 1913, 36, 664. Abst. 'J. Inst. Brewing,' 1914, 20, 78.)

'Colloids as Vehicles of Undesirable Flavour in Beer.' F. Emslander. ('Wochenschr. Brau.' 1913, 30, 387. Abst. 'J. Inst. Brewing,' 1914, 20, 80.)

'Plant Colloids, III.—Processes of Solution and Removal of the Ash of Starch.' M. Samec and F. von Hoefft. ('Koll. Chem. Beihefte,' 1913, 5, 141. Abst. 'J. Inst. Brewing,' 1914, 20, 124.)

'Concentration of Hydrogen Ions in Beer, and its Relation to the Brewing Process.' F. Emslander. ('Zeitschr. Ges. Brauw.' 1914, 37, 2. Abst. 'J. Inst. Brewing,' 1914, 20, 136.)

The colloids of beer migrate towards the cathode. The difference between the concentration of hydrogen ions and the acidity of beer as found by titration is discussed. A form of apparatus is suggested for the measurement of ion concentration for technical use.

'An Account of Some Investigations on the White Wines of South Africa: an Œnological Study.' Horace T. Brown. ('J. Inst. Brewing,' 1914, 20, 345.)

The white wines of the Cape are peculiarly liable to turbidity or 'casse,' accompanied by an increase in colour and a bitter flavour. 'Casse' is not due to micro-organisms, but is conditioned by purely chemical changes, and only arises in contact with air or with oxygen derived from some such source as hydrogen peroxide. The oxidising agent inducing 'casse' does not belong to the class of vegetable oxidases, but consists of a small amount of iron in the ferrous state present in the wine, which behaves as a carrier of oxygen (Fenton's reaction). The 'casse' itself consists of colloidal particles of a combination of iron with products derived from the limited oxidation of tannins and certain proteins present in the wine. The grape contains a peroxidase in the inner cells of the epidermis and in the vascular bundles of the fruit, but freshly expressed grape-juice contains no peroxidase unless the juice of the fruit has remained in contact with the skin for some time. If the amount of oxidase in the juice is considerable it has a tendency to brown on exposure to the air, but there appears to be no connection between the occurrence of oxidase and the *casse ferrique* referred to above.

'Estimation of Colloids in Beers.' R. Marc. ('Kolloid-Zeitschr.' 1914, 14. Abst. 'J. Inst. Brewing,' 1914, 20, 431.)

Measurements made by means of refractometer readings before and after adsorption of colloids by barium sulphate.

'Green Sickness (Verdissement) of Ciders.' Warcollier. ('Comptes Rendus,' 1914, 158, 973. Abst. 'J. Inst. Brewing,' 1914, 20, 457.)

'Variations in the Phosphorus-content of Starch accompanying its Changes of State.' M. Samec ('Kolloidchemische Beihefte,' 1914, **6**, 23. Abst. 'J. Inst. Brewing,' 1914, **20**, 716.)

'Influence of some Colloids on Alcoholic Fermentation.' N. L. Söhngen. ('Folia Microbiologica,' 1913, **2**, 94. Abst. 'J. Inst. Brewing,' 1914, **20**, 720.)

'Retention of Head on Beer.' O. Furnrohr. ('Zeitschr. Ges. Brauw.' 1913, **36**, 473. Abst. 'J. Inst. Brewing,' 1914, **20**, 596.)

'Melanoidines in Roasted Malt.' W. Ruckdischel. ('American Brewers' Journal,' 1915, **39**, 107. Abst. 'J. Inst. Brewing,' 1915, **21**, 123.)

The melanoidines are colloidal condensation products formed during the heating of amino-acids and dextrose present in malted grain.

'The Rate of Adsorption of Various Phenolic Solutions by Seeds of *Hordeum vulgare*, and the Factors Governing the Rate of Diffusion of Aqueous Solutions across Semipermeable Membranes.' Adrian J. Brown and F. Tinker. ('Proc. Royal Soc.' **B.** Vol. **89**, 1915.)

When the osmotic pressures, vapour pressures, and viscosities of a series of solutions of permeable solutes such as the phenols are equal, their rates of diffusion across the barley membrane are inversely proportional to their surface tensions.

'Gluten Turbidity.' E. Moufang. ('Allgem. Zeitschr. für Bierbrau. und Malzfabr.' 1915, **43**, 275. Abst. 'J. Inst. Brewing,' 1916, **22**, 468.)

'Brewers' Filter Pulp.' W. A. J. Foster. ('J. Inst. Brewing,' 1916, **22**, 413.)

'Sensitiveness of Beer towards Cold and the Wallerstein Process.' P. Petit. ('Brasserie et Malterie,' 1916, **6**, 61. Abst. 'J. Inst. Brewing,' 1916, **22**, 468.)

'Pre-mashing and Protein Haze: Concentration of Hydrogen Ions in Beer.' F. Emslander ('Wochenschr. Brauw.' 1916, **33**, 169. Abst. 'J. Inst. Brewing,' 1916, **22**, 509.)

'Selective Permeability: The Absorption of Phenol and other Solutions by the Seeds of *Hordeum vulgare*.' Adrian J. Brown and F. Tinker. ('Proc. Royal Soc.' **B.** vol. **89**, 1916.)

The various solutes enter the barley seeds in an amount which is indicated by the extent to which they are adsorbed by the barley membrane and by the colloidal contents of the seeds. The solutes which are most strongly adsorbed are those which give solutions having low surface tensions and *vice versâ*.

RUBBER.

By Dr. Henry P. Stevens.

Bibliography.

(1) *Composition and Properties of Latex and Raw Rubber.*

'Some Analyses of *Hevea* Latex,' C. Beadle and H. P. Stevens ('The Analyst,' 1911, **36**, 8). Gives the results of analyses of latex from the cortex of the trunks of trees of different ages and also from leaf petioles.

'An Investigation into the Nature and Properties of *Hevea* Latex,' C. Beadle and H. P. Stevens ('8th Inter. Congress of Applied Chem.' Vol. 9, pp. 40-43). Part 1 contains a study of the phenomena accompanying coagulation; distinctions are drawn between the microscopic and macroscopic forms in which coagulation takes place and the effect of formaline on latex. The quantities of acid required for coagulation under different conditions are given. Part 2 contains the results of the chemical analyses of three samples of *Hevea* latex.

'The Carbohydrate Constituents of Pará Rubber,' Pickles and Whitfield ('Proc. Chem. Soc.' 1911, p. 54). It is shown that sheet rubber from *Hevea* latex contains appreciable quantities of l-methyl inositol.

(2) *Production of Raw Rubber.*

The Rubber Growers' Association, 'Revised Tables of Recommendations for the Treatment of Latex and Curing of Rubber,' 1917. The original table has been revised and split up into two tables, one dealing with sheet and the other with crêpe rubber. These tables give concise instructions for the preparation of rubber from the latex, giving proportion of coagulant, preservatives, &c., to be used, types, construction and handling of plant and machinery, instructions for straining, bulking, standard-

ising, coagulating, washing, rolling, drying and sorting, grading, curing, packing, and a list of defects commonly met with and the preventives which can be adopted.

'A Comparison of the Brazilian and Plantation Methods of Preparing Para Rubber,' G. S. WHITBY ('Journ. Soc. Chem. Ind.' 1916, p. 493). Gives the results of comparative tests on rubber prepared in the East by the Brazilian method, smoking and coagulation in thin films, and the typical plantation method of coagulation and rolling to sheets, followed by smoke-drying. Two series of samples were prepared, one from the latex from young trees (five years old) and old trees (fifteen years old). The conclusions arrived at were that the rubber prepared by the Brazilian method was a little inferior to that produced by the plantation method. It was, however, suggested in the discussion following the paper that the Brazilian method of smoking had not been exactly imitated. There was little difference between the rubber from young and old trees. The following conclusions were also arrived at :—Phenols absorbed from the smoke reduce the rate of cure, and, generally speaking, rubber is not improved by smoking, and latex crêpe may be very seriously deteriorated by this means ; 'oxidation' has no ill effect on the quality, and, contrary to the generally accepted view, there is practically no difference in quality between the outer 'oxidised' portion and inner portion of a ball of fine hard Pará.

Comparative tests on rubber from groups of trees in different areas showed marked variation. Also latex allowed to stand before coagulation gave rather better results than that coagulated straight away.

'On the Coagulation of *Hevea* Latex and a New Method of Coagulation,' B. J. EATON and J. GRANTHAM ('Agric. Bull. Federated Malay States,' vol. 4, No. 2 (1915), p. 26). When latex is coagulated spontaneously by exposure to the air there is formed an alkaline scum on the surface where coagulation does not take place, while underneath the serum reacts acid and coagulation is more or less complete (G. S. WHITBY, 'Congress of Applied Chem.' 1912; 'Koll. Zeit.,' **12**, 153). At the same time, strong putrefactive odours develop. The authors find that the putrefactive changes are inhibited while the development of the coagulating agencies have free play if a small quantity of sugar, *e.g.*, 0·2 per cent. dextrine, be added to the latex.

Eng. Pat. 104,323 of 1916, G. M. THOMAS and M. D. MAUDE, claims the process for allowing latex to coagulate spontaneously out of contact with the air, by which the formation of the surface scum is prevented. EATON and GRANTHAM, however, state in the above communication that the coagulation is frequently incomplete when this is effected merely by exclusion of air, whereas in the presence of sugar coagulation is complete either under aërobic or anaërobic conditions. S. MORGAN, however, finds that even in the presence of sugar coagulation is often incomplete (private communication).

Other patents deal mostly with methods of evaporating latex in thin layers, as in native Brazilian Pará.

'Bull. Agric. Intell.' 1915-16, 1703-4. M. KERBOSCH states that rubber obtained by evaporation of latex is less readily oxidised under the influence of sunlight than that produced by coagulation in the ordinary manner.

(3) *The Non-Caoutchouc Constituents of Raw Rubber.*

Nitrogenous constituent.—D. SPENCE was the first to show that the insoluble constituent of rubber (*i.e.*, insoluble in organic solvents such as chloroform, benzene, &c.) was highly nitrogenous, and in fact consisted of protein matter coagulated with the caoutchouc in the latex ('Journ. Liverpool Univ. Inst. of Commercial Research in the Tropics,' No. 13, 1907). Distribution of the protein in Pará rubber.

C. BEADLE and H. P. STEVENS subsequently showed that the nitrogenous or insoluble constituent was necessary for satisfactory vulcanisation, as its removal reduced the proportion of combined sulphur, . d such rubber, vulcanised under normal conditions, had poor physical properties. It was also found that the nitrogenous constituent could be satisfactorily replaced by nitrogenous matter of foreign origin, such as peptone, and less satisfactorily by casein. The choice of nitrogenous substances was limited by the difficulty of incorporating them with the rubber. ('Koll. Zeit.' 1912, **11**, p. 61, 1913, **12**, p. 46 ; 'Journ. Soc. Chem. Ind.' 1912, **31**, p. 1099; H. P. Stevens, 'Koll. Zeit.' 1914, **14**, p. 91.)

D. SPENCE and G. D. KRATZ ('Koll. Zeit.') employ a ·3–·5 per cent. solution of trichloracetic acid in benzene for separating the nitrogenous constituent. When the rubber is swollen in this solvent it rapidly breaks down, giving a solution of low viscosity from which the insoluble nitrogenous constituent is easily separated. Spence examined the

product thus obtained, which contains about 10 per cent. of nitrogen, and regards it as a glycoprotein.

EATON and GRANTHAM found that if freshly coagulated latex be allowed to remain for a few days before washing or rolling the rubber eventually obtained is rapidly-curing and possesses considerably superior physical properties after vulcanisation ('Agric. Bull. F.M.S.' 1915, **3**, p. 442, and **4**, p. 58, also 'Journ. Soc. Chem. Ind.' 1916, **35**, p. 715). This increase in rate of cure they attributed to some accelerating substance formed in the rubber by the action of micro-organisms, as they found that freezing the rubber inhibited the development of the rapid-curing properties, but these were restored on allowing the temperature to rise again. Further, formalin and other antiseptic treatment, *e.g.*, smoking, had also an inhibiting effect. They also observed that once the rapid-curing effect was produced, this was not destroyed by heating to relatively high temperatures, as in the treatment of the rubber in a hot-air drier or by washing on crêpeing rolls.

J. GRANTHAM ('Agric. Bull. F.M.S.' **4**, pp. 1-4) published a number of nitrogen determinations of plantation rubber and concludes that smoking appears to fix the nitrogen. Generally speaking, matured 'slab' gave low figures, especially after crêpeing, in spite of the rapid-curing properties of this rubber.

H. P. STEVENS confirmed Eaton and Grantham's results and succeeded in separating the accelerating substance, which was found to be an organic base or mixture of bases formed during putrefaction. The rapid-curing properties were found to be partly, but not completely, removed by washing on crêpeing rollers. ('Journ. Soc. Chem. Ind.' 1917, **36**, p. 365.) Larger quantities of base could be extracted from rapidly-curing rubber than from slow-curing rubber. The bases can also be obtained from the latex serum and produce acceleration of vulcanisation when added to ordinary crêpe.

Synthetic organic accelerators.—A general description of organic accelerators for vulcanisation and their characteristics have appeared at various times (Ditmar, 'Gummi Zeitung,' 1915, **29**, p. 425; Gottlob, 'Gummi Zeitung,' 1916, **30**, p. 303; A. H. King, 'India Rubber Journ.' 1916, **52**, p. 440; S. J. Peachey, 'I.R.J.' 1916, **52**, p. 603; S. J. Peachey, 'Journ. Soc. Chem. Ind.' 1917, **36**, p. 424). The first patent of importance is given as that of Bayer & Co., Elberfeld Farbenfabrik, Ger. Pat. 265,221 of Nov. 16, 1912. This was for the use of piperidene. Subsequently it was recognised that all organic bases act as accelerators, but that only those having a high dissociation constant are sufficiently powerful for technical work. This led to the patent taken out by Bayer & Co., claiming all organic bases having a dissociation constant greater than 1×10^{-8} (Ger. Pat. 280,198 of 1914). S. J. Peachey has patented the nitroso-derivatives of certain bases (Eng. Pat. 4,263 of 1914), particularly *p*-nitroso-dimethyl aniline, which differ from compounds previously referred to in that they are not strong bases and are yet very effective accelerators. Peachey has also patented condensation compounds formed by the interaction of aldehydes and amines (Eng. Pat. 7,370 of 1914), but these substances are not so powerful as the nitroso-derivatives.

D. SPENCE ('Journ. Soc. Chem. Ind.' 1917, **36**, p. 118) claims to dispose of the novelty of all these inventions, and states that, six months previous to the date of application of the Bayer patent of 1912 (covering the use of piperidene), he described experiments in which piperidene was used in the 'Kolloid Zeitschrift,' 1912, **10**, pp. 303-305.

DUNLOP RUBBER Co. and TWISS (Eng. Pat. 1916, 17,756) have patented the use of caustic soda or potash in solution in glycerol as a vulcanising accelerator. The accelerating effect of mineral bases is well known, particularly lime and magnesia. The glycerol is used as an agent for incorporating the alkali in the rubber (see also paper by D. F. Twiss ('Jour. Soc. Chem. Ind.' 1917, **36**, 782).

Resinous constituent.—L. E. Weber, 'The Action of Resins in the Vulcanising of Rubber' ('Inter. Congress of Applied Chem.' 1912, **9**, 95). The author prepared three compounds from the same mixing, containing rubber, litharge, sulphur, and whiting, as follows:—Compound A was prepared with plantation-smoked sheet, which had been cut up and extracted for fifteen hours with acetone. Compound B exactly resembled the foregoing except that the rubber was used without previous extraction. Compound C was identical with compound B except that it contained in addition the resins (acetone extract) obtained from the rubber used for compound A. On vulcanising (in water) it was found that compound A 'could not be vulcanised,' that is to say, cured for one hour at 140° C.; 'it showed a strength of less than 20 lb.,' while compounds B and C variously cured gave figures up to 800 lb. with irregular differences. The author

concludes that 'the resins play an active part in the vulcanisation and not merely the part of catalyser. Their presence is absolutely essential.'

C. Beadle and H. P. Stevens, 'The Nature of the Resinous Constituent and its Influence on the Quality of Rubber' ('Inter. Congress of Applied Chem.' 1912, **25**, 581). The authors made comparative vulcanising tests with *Hevea* and Rambong (*Ficus elastica*) rubbers, one compound prepared from acetone (or alcohol) extracted rubber and the other from the untreated rubber. The compound employed consisted of the rubber (treated or untreated) and sulphur without other ingredients. They noted that the compound prepared from the extracted rubber appeared undercured when compared with a control specimen of untreated rubber, but the main difference between the vulcanised samples was shown on keeping the vulcanised specimens, when those prepared from the extracted rubber rapidly hardened and deteriorated (perished).

H. P. Stevens, 'The Function of Litharge in the Vulcanisation of Rubber,' Part II., 'The Influence of the Resinous Constituents' ('Journ. Soc. Chem. Ind.' 1916, **35**, p. 874). The author describes further comparative tests with resin-extracted rubber, using compounds with and without litharge and determining the coefficient of vulcanisation.

(4) *Vulcanisation.*

Spence and his collaborators ('Koll. Zeit.' 1911, **8**, 304, **9**, 83, 300; 1912, **10**, 299; **11**, 28, 274; 1913, **13**, 265).—The process of vulcanisation is studied in a systematic series of experiments, and the conclusions arrived at point to vulcanisation as essentially a chemical reaction between sulphur and the caoutchouc, the amount of combined sulphur being proportional to the time of heating with a temperature coefficient of approximately 2·7 for a rise of 10° C. Moreover, when the amount of sulphur is limited (*e.g.*, 10 per cent. on the caoutchouc), the whole becomes combined on prolonged heating, and with an excess of sulphur the maximum combined sulphur corresponds approximately to the formula $C_{10}H_{16}S_2$ (compare also C. O. Weber, 'The Chemistry of India Rubber,' pp. 87-91; also Hinrichsen and Kindscher, 'Gummi Zeit.' 1903, **18**, 251; 'Koll. Zeit.' 1912, **11**, 191; 'Ber.' 1913, **46**, 1291).

Skellon, in more recent work, gives a great amount of data which confirms the above ('Koll. Zeit.' 1914, **66**, p. 96; 'The Rubber Industry papers read at the Exhibition held in London in 1914,' p. 172).

F. W. Hinrichsen and K. Meizenberg ('Ch. Zeit.' 1909, **33**, p. 756). Quantitative experiments on cold vulcanisation.

E. Stern ('Ch. Zeit.' 1909, **33**, p. 256), 'Study of the Reaction between Rubber and Sulphur in Solution in Naphthalene.'

Harries and Fonrobert ('Ber.' 1916, **49**, 1196 and 1390). Rubber was vulcanised in sheets 6 mm. thick by heating a mix containing 10 per cent. of sulphur for thirty minutes at 145° C. After sixty days' extraction with hot acetone, only 0·25 per cent. sulphur remained, and it is concluded that this would have been removed if the extraction had proceeded long enough. It is therefore concluded that vulcanisation is a physical change. A distinction, however, is drawn between vulcanisation as carried out above, which the authors term 'primary vulcanisation,' and the more fully vulcanised product obtained by longer heating or by 'after-vulcanisation' of the primary vulcanised body.

D. F. Twiss ('Journ. Soc. Chem. Ind.' 1917, **36**, 782). This paper contains a review of the subject and a very full reference list. The original work contained in it deals particularly with the relative reactivities of $S\mu$ and $S\lambda$ as vulcanising agents. It is concluded that the modification in which the sulphur is employed is practically without influence on the course of vulcanisation. Compare also Dubosc ('Le Caoutchouc et la Gutta Percha,' Jan. 1917).

I. I. Ostromyslenski ('Journ. Russ. Physico-Chem. Soc.' 1915, **47**, 1453 *et seq.*, 1885 *et seq.*; also

Vulcanisation of caoutchouc by means of halogen compounds, and mechanism of the vulcanisation process.	'Journ. Soc. Chem. Ind.'	1916,	**35**,	370
Hot vulcanisation of caoutchouc by means of nitro-compounds in absence of sulphur.	,,	,,	,,	,,	59
Hot vulcanisation of caoutchouc by means of peroxides or per-acids, in absence of sulphur.	,,	,,	,,	,,	59

Cold vulcanisation of caoutchouc by means of sulphur, trinitrobenzene, or benzoyl peroxide.	'Journ. Soc. Chem. Ind.'	1916,	35,		369
Mechanism of vulcanisation of caoutchouc.	,,	,,	,,	,,	59
Mechanism of action of amines and metallic oxides on the vulcanisation of caoutchouc.	,,	,,	,,	,,	370
Vulcanisation of caoutchouc by molecular oxygen, ozone, or organic ozonides.	,,	,,	,,	,,	370
Vulcanisation of synthetic caoutchouc.	,,	,,	,,	,,	58
Preparation of vulcanised caoutchouc coloured by organic colouring matters.	,,	,,	,,	,,	371
Process for obtaining a substance identical with or analogous to natural vulcanised rubber.	,,	,,	,,	,,	131

I. I. OSTROMYSLENSKI and I. M. KELBASINSKAJA ('Journ. Soc. Chem. Ind.' **35**, 58, 'New Constants of Caoutchouc, Elasticity Point and Fatal Temperature').

The first three papers describe methods for producing a vulcanised rubber without the use of sulphur by heating the rubber (*a*) with nitro-aromatic derivatives, *e.g.*, trinitrobenzene, or (*b*) with organic peroxides, *e.g.*, benzoyl peroxides.

H. P. STEVENS ('Journ. Soc. Chem. Ind.' 1917, **36**, 107) has shown that reaction (*a*) only proceeds in the presence of a base such as PbO or MgO, and that the products are inferior technically to rubber vulcanised with sulphur. Compare also Twiss (p. 63).

H. HEILBRONNER and J. BERNSTEIN ('Rubber Industry,' 1914, 156; 'Caoutchouc et Gutta Percha,' 1915, **12**, 8720) describe a method of vulcanisation in which rubber and sulphur in solution are exposed to the action of ultra-violet light from a quartz mercury vapour-lamp. Once the solvent has evaporated from this solution the rubber becomes insoluble.

(5) *Physical Testing of Vulcanised Rubber.*

P. L. WORMELEY ('Rubber Industry,' 1914, 246-256). This paper brings out the great influence exerted by temperature on the results of physical tests.

P. SCHIDROWITZ ('Rubber Industry,' 1914, 230-245), 'Outline of a Method of Physical Tests.'

H. P. STEVENS ('Journ. Soc. Chem. Ind.' 1916, **35**). Criticises current methods of testing, particularly with regard to state of cure of the specimens tested and the ageing factor.

A. VAN ROSSEM ('Bijdrage tot de Kennis van het vulcanisatieproces,' Amsterdam, 1916) contains the results of tests on a very large number of vulcanised rubber samples, with mathematical treatment of same.

See also publications of the International Association for Rubber Cultivation in the Netherlands Indies, Delft, Part I., published in 1917; 'Bulletin of Imperial Institute,' 1916, **14**, 495.

(6) *Synthetic Rubber.*

I. I. OSTROMYSLENSKI ('Journ. Russ. Phys.-Chem. Soc.' 1915, **47**, 1441 *et seq.*, 1928 *et seq.*; 1916, **48**, 1071 *et seq.*

Condensation of alcohols and aldehydes in presence of dehydrating agents.	'Journ. Soc. Chem. Ind.'	1916,	35,		69
New syntheses of caoutchouc and its homologues.	,,	,,	,,	,,	368
Mechanism of transformation of isoprene and β myrcene into caoutchouc.	,,	,,	,,	,,	369
Production of caoutchouc.	,,	,,	,,	,,	130
Constitution of caoutchoucs.	,,	,,	,,	,,	369
Definition, classification and evaluation of caoutchoucs.	,,	,,	,,	,,	57
New methods of preparation of divinyl, isoprene, piperylene, and dimethyl-erythrene.	,,	,,	,,	,,	380
Formation of erythrene.	,,	,,	,,	,,	69
New methods of preparation of erythrene.	,,	,,	,,	,,	69

Transformation of cyclobutane derivatives into erythrene.	'Journ. Soc. Chem. Ind.' 1916, **35**,				381
Synthesis of the symmetrical bromide of erythrene-caoutchouc, of caoutchouc itself and of caouprene.	,,	,,	,,	,,	368
Preparation of esters of unsaturated alcohols from aldols.	,,	,,	,,	,,	382
Polymerisation of ethylenic compounds and mechanism of transformation of vinyl bromide into bromide of erythrene-caoutchouc.	,,	,,	,,	,,	369
Analysis, purification, and reactions of isoprene.	,,	,,	,,	,,	381
Polymerisation of isoprene, divinyl and dimethylerythrene to caoutchouc or its homologues.	'Journ. Chem. Soc.' 1917, **112**,				i. 399
Preparation of substances equivalent to ebonite, celluloid or gutta percha. Synthesis of vulcanised caoutchouc.	,,	,,	,,	,,	i. 403
Synthesis of the symmetrical chloride and of the higher chloride of erythrene caoutchouc. New chlorides of natural isoprene and erythrene caoutchoucs. ('J. Russ. Phys. Chem. Soc.' 1916, **46**, 1132-1151.)	,,	,,	,,	,,	i. 404

B. D. W. Luff ('Journ. Soc. Chem. Ind.' 1916, **35**, 983). 'Some Aspects of the Synthesis of Caoutchouc.'

Kondakow ('Caoutchouc et Gutta Percha,' 1917, July 15). Deals historically with his own researches.

Note.—'Rubber,' by Dr. H. P. Stevens, forms one of the sections in the 'Annual Reports on Industrial Chemistry,' vol. i., issued by the Society of Chemical Industry.

COLLOID CHEMISTRY OF STARCH, GUMS, HEMICELLULOSES, ALBUMIN, CASEIN, GLUTEN, AND GELATINE.

By H. B. Stocks, *F.I.C.*

Starch.

The application of starch in the sizing and finishing industries, for which it is used in very large quantities, depends entirely upon its colloidal properties. That is, on heating with water, it forms a plastic mass, or adhesive sol, according to the concentration and the temperature. It can therefore be readily applied to textile fibres or fabrics. In the sizing industry it is applied to the yarn—the warp—to strengthen it, render it smoother (*i.e.*, lay the individual fibres), and thus facilitates weaving, while in heavy sizing it acts as a binder to hold the weighting material, usually china clay, which is employed. For these purposes, although very useful, it is not altogether perfect, since, on drying, it does not form a continuous film. In calico-printing it is one of the mediums employed for carrying or thickening the colours, thus preventing them spreading into the surrounding tissues. For these purposes potato starch or farina, wheat-starch and wheat-flour, sago, tapioca, maize, cassava, and rice-starch are employed.

It is well known that the granules of the various starches vary in appearance under the microscope, they also vary somewhat in their properties; for instance, sago, tapioca, and cassava starches yield more

tenacious or glutinous sols than the others, and for particular purposes certain starches may be found more suitable than others.

Starch absorbs a certain amount of water from the atmosphere; this varies with the conditions, but is usually from 13 to 15 per cent.; it also contains a small proportion of mineral matter, which is, in all cases, alkaline; this amounts in potato-starch to about 0·22 per cent., sago 0·4, cassava 0·12, maize 0·11, and wheat 0·23, therefore in dealing with natural starch we have to take into account the influence the electrolytes in this mineral matter will have upon the starch molecules.

On heating with water no action whatever is apparent until a temperature of about 55° C. is reached, when it is noticed that a few granules have swollen enormously; from this point onwards there is a progressive increase in the number of swollen granules, till at a certain temperature all the granules have become fully hydrated and most, if not all, have burst, although the granules can still be observed more or less distorted. The temperature at which this occurs is the maximum thickening-point of the mixture, this occurring with wheat-starch at 65° C., maize 70°, sago 72°, rice 74°, and potato-starch 63°.

The viscosity of solutions made from different starches varies; thus, G. M. MacNider ('Journ. Ind. and Eng. Chem.' 1912, **4**, 417–422) found the viscosity of potato-starch to be 14·31, maize 2·49–2·86, cassava 3·88–3·97, wheat 1·24–1·26, and rice 1·00 for solutions containing 12 grams in 30 c.c. of water. These figures need verification, as the differences appear to be very much greater than one would suppose possible, although, no doubt, a certain amount of variation does really exist. It was noted also by the above observer that very small quantities of borax (*i.e.*, ·08 gram) and of caustic soda (·06 gram) lowered the viscosity, while larger quantities (*i.e.*, 1·0 gram) increased it, the viscosity being also lowered by boric acid.

Since writing the above, the author has found that the time factor is most important. For instance, freshly prepared and quickly cooled potato-starch solution of 2 per cent. concentration gave the following figures (water = 1) :—

Fresh.	5 min. later	40 min. later.	18 hours later
106·7	96·3	19·3	1·3

At the last period quite a considerable quantity of the starch granules had deposited, leaving a clear liquid on the surface, which could be filtered.

The viscosity of starch solution does not therefore increase, as with other colloids, with the time.

It was at one time believed that starch granules consisted of two distinct substances, an inner material or granulose (amylose), and an outer material named starch cellulose or amylopectin; but according to Harrison ('Journ. Soc. Dyers and Colourists,' 1916, **32**, 40–44) the outer portion of the starch granules does not differ in composition from the inner material although it is more resistant to hydrolytic agents. By physical means alone they are capable of being changed one into the other. Z. Gatin-Gruzewska and L. Macquenne ('Compt. Rend.' 1908, **146**, 540–545) also conclude that there is a structural relationship between amylose and amylopectin, and that probably each is composed of a series of closely related substances.

The addition of certain substances to starch and water lowers the surface tension of the granules so that the thickening-point is more or less depressed; this is especially the case with caustic soda, zinc chloride, and

hydrochloric acid, which in concentrated solutions form a tenacious white translucent gel with starch even at the ordinary temperature; other metallic chlorides behave similarly to zinc chloride, although less marked in their action, but the chlorides of the alkalies appeared to be without effect. Gels made on these lines, containing 9 to 34 per cent. of starch, 4 to 20 per cent. of zinc chloride, and 0 to 19 per cent. of magnesium chloride, are sometimes sold for sizing purposes (H. B. Stocks and H. G. White, 'J.S.C.I.,' 1903, 22, and 'Jour. Soc. Dyers and Colourists,' March 1894).

E. Fouard ('Comp. Rend.' 1907, **144**, 501–503 and 1366–1368) found the amount of phosphoric acid in a starch containing 0·331 per cent. of ash to be 0·1915 per cent. By treatment with acid these were reduced to 0·123 and 0·1117 per cent. respectively, and he is of opinion that the acid is absorbed by the insoluble starch granule. Acids have a coagulating effect upon starch in proportion to their hydrogen-ion concentration, very weak acids having no appreciable effect. Alkalies, on the other hand, have an exactly opposite effect, either dissolving the starch or decreasing its tendency to coagulation, the retardation being strictly in proportion to their hydroxyl-ion concentration. Salts which hydrolyse in solution act upon starch in one or other of these directions according to the predominance of the hydrogen or hydroxyl-ions respectively. This coagulating effect of the hydrogen-ions and the swelling effect of the hydroxyl-ions is general throughout the whole of the organic and some of the inorganic colloids, and is a capillary phenomenon of the greatest importance.

The mineral matter of starch can be to a certain extent removed by precipitating a dilute sol with alcohol, or, better, by addition of ammonium carbonate. Sols of starch purified by these means are very unstable, the starch reverting to the insoluble form in very minute granules on standing. W. Harrison ('Jour. Soc. Dyers and Colourists,' 1916, **32**, 40–44), also L. Macquenne ('Compt. Rend.' 1908, **146**, 317–318), G. Malfitano and A. Moschkoff ('Compt. Rend.' 1910, **150**, 710–711), by successive freezing and thawing of solutions of starch, have obtained it almost free from mineral matter which remained in solution in the water. The starch thus prepared formed a heterogeneous mixture with water even after heating, and on standing the starch settled out again. These authors believe that starch is entirely insoluble in water but that in association with electrolytes it forms colloidal solutions.

The Arabol Man. Co. (Fr. Pat. 394,167, 1908) use KCNS for preparing starch soluble in cold water, while, according to W. Lenz ('7th Int. Cong. Appl. Chem. Lond.' 1909), sodium salicylate causes some starch granules, though not all, to swell.

Starch adsorbs alkalies and alkaline earths; the adsorption compounds, although unstable in water, appear to be more stable in contact with alcohol; thus starch precipitated from a solution in caustic potash by alcohol contains potassium in proportion to the strength of the caustic potash solution (E. Fouard, 'Bull. Soc. Chim.' 1909, **5**, 828–834). Precipitation of starch in presence of barium hydroxide by means of alcohol has also been proposed by Asboth ('Analyst,' July 1887; also 'Jour. Soc. Chem. Ind.' 1888, 77) as a method of estimating this substance by volumetric means, the compound containing 19·1 per cent. of BaO, corresponding with the formula $C_{24}H_{40}O_{20}BaO$. In order to get concordant results it is necessary that certain conditions as to strength of reagents, &c. should always be complied with. According to W. Harrison ('Jour. Soc. Dyers

and Colourists,' 1916, **32**, 40–44), the composition of the precipitate varies with the concentration of the barium hydrate according to the laws of adsorption. According to Tollens, starch combines with Na or K in the proportion of 1 atom to 4 ($C_6H_{10}O_5$); on addition of alcohol amorphous precipitates with alkaline reaction are formed; these are represented as potassium starch $C_{24}H_{39}O_{20}K$ and sodium starch $C_{24}H_{39}O_{20}Na$.

On heating starch with caustic alkalies a change takes place with the scission of acetic acid, the amount of alkali neutralised when N strength of solution is employed being equal to 8·33 per cent. of KHO. A similar change takes place with all carbohydrates, but the amount of acid liberated varies very considerably, pointing to differences in structural arrangement.

The stiffening power of starch appears to depend upon the amount of swelling to which individual starches are liable on heating with water; in other words, to the extent of the dispersion; thus, by heating to a few degrees above the temperature of swelling and centrifuging the sol, W. Harrison ('Jour. Soc. Dyers and Colourists,' 1911, **27**, 84–88) found the volume of the swollen granules to be directly proportional to the stiffening power, the experiments agreeing closely with the formula

$$\text{Viscosity} = 1 + (4{\cdot}75 \times \frac{\text{Vol. of granules}}{\text{total vol. of solution}});$$

alkalies if present cause high results, as might be expected.

Starch gel on standing separates into two phases, a more solid gel and a liquid phase, the latter containing very little starch; several other colloids behave in a similar way, notably cellulose xanthate or viscose; some colloids, such as gelatine, do not behave in this manner. The phenomenon is probably due to the aggregation of the molecular complexes, the colloid becoming less dispersed. Starch shows practically no osmotic pressure (*i.e.*, only 2 m.m. at 13° for a 1 per cent. solution) in a parchment paper diaphragm (Moore and Roaf, 'Biochem. Jour.' **II.** 39), neither does it show any appreciable depression by the freezing-point method of Raoult, pointing to a very high molecular weight (E. Fouard, 'Compt. Rend.' 1908, **146**, 978–981). On the other hand, pure soluble starch, according to L. Macquenne ('Compt. Rend.' 1908, **146**, 317-318), passes through filtering material, even the Chamberland filter, and E. Fouard ('Compt. Rend.' 1908, **146**, 285–287) found that a solution containing 2·74 per cent. of pure starch could be filtered through a collodion membrane. The molecular solution volume is lower than that calculated by Taube's method ('Ber.' 1895, **28**, 410), *i.e.*, 92·6–93·3 instead of 102·6 (Cross and Bevan, 'Ber.' 1909, **42**, 2,198–2,204), which the authors regard as evidence of ring-formation. Other colloids show a similar result.

With regard to the action of reagents, other than those mentioned, upon starch, it is capable of forming a xanthic derivative in the same way as cellulose by action of caustic soda and carbon bisulphide (C. F. Cross, J. F. Briggs, and Société Française de la Viscose, Fr. Pat. 370,505, 1906), while a nitro-derivative of starch has been suggested as a substitute for celluloid (G. E. Arnold, A. S. Fox, A. C. Scott, and H. E. V. Roberts, Eng. Pat. 3,450, 1906).

Oxidising agents have a marked effect upon starch (see soluble starch). F. G. Perkins (U.S. Pat. 1,020, 656, 1912) proposes to prepare a glue from cassava starch by acting upon it with sodium peroxide and caustic soda.

Starch and tannic acid mutually precipitate each other, this being also

the case with soluble starch and dextrin, but in lessening degree. This fact should be borne in mind in testing a colloid for gelatine by means of tannic acid.

Ordinary wheat-flour is used very largely for sizing purposes, both in its fresh state and after long-continued fermentation. It differs from the starches in containing the nitrogenous colloid gluten, a coagulable albumen, sugar, dextrin, &c. It is doubtful if in the fresh state the gluten exerts any marked influence, but during fermentation the gluten, which suffers little in the process, becomes dispersed and forms a colloidal solution in the acids, which are generated, thus becoming available as a binding agent; other marked changes also take place (H. B. Stocks, 'Jour. Soc. Dyers and Colourists,' 1912, **28**, 148–151, also H. B. Stocks and H. G. White, 'Jour. Soc. Chem. Ind.' 1903, **22**).

Soluble Starch.

The so-called 'soluble' starch may be formed from ordinary starch in a variety of ways, the processes which have been proposed falling naturally into certain classes.

1. By heating starch at a regulated temperature but lower than that which will convert it into dextrin.

2. Heating starch with water under pressure (H. Hale, Eng. Pat. 3,311, 1866).

3. Treating starch with acids, J. Sellars (Eng. Pat. 2,810, 1865) proposed to heat the starch with a mineral or vegetable acid, then neutralise with soda. Rellmas steeps starch in a 1 to 3 per cent. solution of a mineral acid at 50° to 55°. Fols carries out the same process at 80° C. A. Schuhmann (Eng. Pat. 5,460, 1887) treats starch with acid in the cold, washes out the acid, and heats with SO_2 under pressure. W. P. Thompson (A. H. J. Berge, Eng. Pat. 7,272, 1891) employs SO_2 under pressure, while W. Thompson and J. Morris (Eng. Pat. 21,973, 1906) claim to employ SO_2 at 200°–220° F. H. H. Lake (W. Angelo, Eng. Pat. 5,617, 1893) treats starch with strong HCl and dries at a low temperature. G. Rivat (Fr. Pat. 433,726, 1910) claims the application at 100° C. of dilute solutions of H_3PO_4,HF, potassium bitartrate, acid potassium oxalate, or aromatic sulphonic acids. Reumer (Eng. Pat. 10,873, 1902) proposed the application of organic acids at 115°, while Cross and Traquair (Eng. Pat. 9,868, 1902) claimed the application of carboxylic acids, such as acetic or formic, but specially the former, together with dehydrating agents, *e.g.*, alcohol or concentrated solutions of salts. The amount of glacial acetic acid employed is from one-third to one-half the weight of the starch, and they claim that under these conditions an acetyl derivative of starch is formed. The product has been named 'feculose' (see also Traquair, 'Jour. Soc. Chem. Ind.' 1909, 288).

4. *Oxidising agents.*—Starch is treated with chlorine or calcium hypochlorite (C. H. Meyer, Eng. Pat. 1,146, 1893), with hypochlorite or chlorate of potassium or sodium (C. Brender, Eng. Pat. 17,650, 1898). A. Ashworth (Eng. Pat. 19,720, 1901) treats starch with acid and a chlorate, with or without the addition of a catalytic agent, *e.g.*, vanadium chloride, $CuSO_4$, or $CuCl_2$. Siemens and Halske (U.S. Pat. 798,509, 1905) propose the use of chlorine gas; the use of acids, such as HCl, H_2SO_4, and organic acids, is also mentioned in the specification. Chlorine is claimed by H. Kindscher (Ger. Pat. 168,980, 1902). In W. von Siemens and C. Witt's

patent (Eng. Pat. 24,455, 1895) it is proposed to treat first with $K.MnO_4$, then by HCl, and finally to remove excess of Cl, by means of SO_2, or a dilute solution of a bisulphite. The soluble starch is stated to form a clear filterable solution with dilute potash solution.

F. Fritsche (Eng. Pat. 1,351, 1908) claims the application of perborates for the preparation of soluble starch; perborate of soda is also used for rendering starch, gums, algæ, lichens, &c., soluble by heating (Stolbe and Kopke, Fr. Pat. 384,704, 1907, and addition Jan. 23, 1908); F. G. Perkins (U.S. Pat.—1,020, 656—1912) uses sodium peroxide for rendering starch soluble.

5. *Alkalies.*—J. Kantorowitz (Eng. Pat. 5,844, 1896) claims the preparation of soluble starch by treating ordinary starch with NaHO, neutralising with HCl, and precipitating the product with $MgSO_4$ or by keeping at a temperature of 20° C. for several hours. In a later patent (Eng. Pat. 10,216, 1910) Kantorowitz claims the application of caustic soda, but to prevent the former swelling the reaction is carried on in presence of concentrated solutions of salts, *e.g.*, Na_2SO_4.

6. *Treatment with neutral salts.*—Soluble starch can be formed by heating starch with a strong solution of KCNS and alcohol, the latter probably added to prevent swelling, as in the last example. (The Arabol Man. Co., Fr. Pat. 394,167, 1908.)

C. F. Cross and J. S. Remington (Eng. Pat. 1,035, 1899) propose to use the fruit of the horse-chestnut as a source of starch or soluble starch.

Soluble starch does not differ in appearance from ordinary starch, except that in some cases the hilum of the granules appears to be fractured. On heating with water, however, it behaves quite differently; thus 1 part of ordinary starch heated with 9 parts of water yields a stiff white paste, which on cooling becomes a white opaque gel from which after a time water separates. On the other hand, soluble starch in the same proportion forms a thin opalescent but nearly clear sol which remains fluid on cooling, for which reason it is known as thin-boiling starch. The change which has taken place is probably largely one of de-polymerisation.

M. Saurec and S. Jencic ('Koll. chem. Beihefte,' 1915, **7**, 137–171) state that the formation of soluble starch is accompanied by a reduction in the size of the molecule, but this is not always the case. Dextrin is almost always present, although it is claimed that in certain products it is absent. The soluble starches usually, although not invariably, contain a higher mineral content than ordinary starch, amounting to about 1·5 per cent., and this being alkaline will have a decided effect upon their properties; the amount of water is also higher, *i.e.*, 17 to 21 per cent. Soluble starch on heating with caustic alkali yields a higher percentage of acetic acid, *i.e.*, about 13 per cent. of KHO is neutralised, pointing to a molecular change. It is precipitated by tannic acid, but to a lesser extent than ordinary starch. Soluble starch reverts to the insoluble form when a solution is allowed to stand (E. Fouard, 'Compt. Rend.' 1908, **147**, 931–933). Soluble starch is used in sizing and finishing, but more particularly for the latter purpose; it yields a continuous film and imparts a 'fuller' feel to fabrics than does ordinary starch.

Dextrin.

The products sold under the name of dextrin or 'British gum' vary very widely in their properties, being complexes of true dextrin, soluble

starch, possibly unaltered starch and glucose. There appear to be several modifications of dextrin, known as erythrodextrin, amylodextrin, achrodextrin, &c., which differ from each other in their molecular weights.

Pure dextrin can be prepared by dissolving starch in moderately concentrated sulphuric acid, quickly neutralising with alkali and precipitating with alcohol.

The commercial dextrins are prepared by heating dry starch either alone or after sprinkling with nitric acid to temperatures between 100° and 280° C. Nitric acid or a mixture of nitric and sulphuric acid are used (W. S. Hayward, Eng. Pat. 2,612, 1858). It is also produced by the restrained action of malt extract upon starch (B. J. B. Mills (T. Sim and E. S. Hutchinson), Eng. Pat. 933, 1869). The products vary according to the method of treatment, white dextrin containing soluble starch and possibly unaltered starch, while brown dextrin contains more or less glucose.

Dextrin contains about 12 per cent. of water and about 0·2 per cent. of mineral matter. On heating with normal alkali solution the acetic acid liberated neutralises 15 to 24 per cent. of KHO. According to G. Malfitano and A. Moschkoff (' Compt. Rend.' 1912, **154**, 443–446), starch is converted into dextrins by drying over P_2O_5. When the desiccation is prolonged so that the water of constitution is removed the solubility is diminished. They regard the molecule of starch as consisting of $C_6H_{10}O_5$ aggregates linked together by OH.H molecules and that by the loss of the latter the molecule becomes disintegrated.

Dextrin is only slightly precipitated by tannic acid; it is precipitated readily by alcohol, but is not readily salted out by electrolytes, only concentrated solutions of sulphates and not those of other salts causing it to separate (S. Levites, ' Zeit. Chem. Ind. Kolloide,' 1908, 3, 145–153).

Dextrin is used to a considerable extent in finishing and calico-printing, imparting a very hard ' boardy ' feel to cloth, which for certain purposes is much desired. It is also employed as an adhesive under the name of British gum, in place of gum arabic, but the solutions have much less viscosity, and therefore stronger sols have to be employed. It has, however, two advantages, that is, it can be spread in a thinner layer and is more readily softened when moistened; for these reasons it has largely replaced the natural gum. It is remarkable that, although a profound modification must have been made by treating starch at high temperatures, the structure of the granules is in no way affected until water is added, when they entirely dissolve. It is used to some extent in painting (Church, ' Chemistry of Paints and Painting,' p. 72), but it is rarely used for emulsifying purposes.

Pfeffer, using a membrane of copper ferrocyanide, found the osmotic pressure of dextrin to be 16·6 c.m. of mercury (Ostwald, ' Solutions,' p. 94); Musculus and A. Meyer (Bull. Soc. Chim., **30**, 370) found the rate of diffusion of dextrin through membranes to be for Y dextrin (achroodextrin) 7, and amylodextrin, 1; dextrose hydrate being taken as 100.

Barium oxide is adsorbed by commercial dextrins, but it has been found that the amount varies with the percentage of starch present, the following results having been obtained:

	Starch.	BaO adsorbed
Dextrin 1 . . .	1·99	1·75
„ 2 . . .	13·13	3·53
„ 3 . . .	24·72	5·64
Starch	100·0	23·61

Gum Arabic.

The commercial gum arabic is often a mixture of gums from several species of trees, and is therefore a variable product. The best gum arabic is that obtained from *Acacia Senegal*, known as Hashab gum, which comes from Kordofan and the Blue Nile District. Gums are also obtained from several other species of acacia, and, although these resemble gum arabic in appearance, they differ from it more or less in constitution and also notably in yielding solutions which are less viscous and much less adhesive. They therefore rarely appear in commerce except in admixture as above stated.

Gum arabic contains normally about 15 per cent. of water and 3½ per cent. of mineral matter, which consists largely of the carbonates of potash and lime. It has long been regarded as an acid—arabic acid—in combination with bases. The same acid is supposed to be present in beet-root juice. More recently the researches of O'Sullivan and others have, according to H. H. Robinson ('Report on the Chemistry of Gums,' British Association, 1906), appeared to prove that the gums are composed of complex acids built up of a nucleus acid associated with the sugars galactose, arabinose, and xylose. Arabic acid is the nucleus acid in gum arabic and geddic acid in gedda-gum. Without subscribing to this decision, it may be stated that gum arabic functions as an acid, and either combines with or adsorbs metallic bases; it is a complex of the two carbohydrates galactan and araban.

Gum arabic is employed more for its adhesiveness than for any other property, but closely allied to adhesiveness is viscosity, the gums which yield the most viscous solutions being the most valuable. It is employed in painting (Church, 'Chemistry of Paints and Painting') as a glaze or varnish, in the manufacture of sweets, and for emulsifying oils, for which purposes it is eminently fitted.

Gum arabic is usually entirely soluble in water. The gum from the earliest exudation is, however, not entirely soluble, yielding a glairy mucus-like fluid, from which a perfect solution separates after a time. After storage for two to three months a change has taken place in the product, probably due to enzymes, so that it dissolves entirely (F. Reinitzer, 'Zeitschr. f. Physiolog. Chem.' 1909, 352–392, also '3rd Report of the Wellcome Research Laboratories, Khartoum'). Dr. Beam ('2nd Report of the Wellcome Research Laboratories') notes the fact, which, however, was previously well known, that the viscosity of a solution prepared in the cold is greater than when heat is employed. It may be mentioned that gum arabic contains at least three enzymes, an oxidase, a peroxidase, and a diastase (F. Reinitzer, 'J. Physiol. Chem.' 1909, **61**, 352-392), the functions of which have not yet been determined, but these render the gum incompatible for use with several medicinal preparations; incidentally they also serve for detecting gum arabic in admixture with other gums, *e.g.*, tragacanth, which are free from these enzymes.

Hashab gum was found to be composed of two gums, a hard and a soft one. On exposure to the sun the hard gum remains glassy, but the soft kind becomes white and opaque, owing to the development of innumerable tiny fissures. By this treatment it appears to be bleached, although this is really not the case. There is a marked difference in the

viscosities of the two varieties in the torsion viscosimeter, a 20 per cent. solution of the hard gum indicating a retardation of 60 to 70 deg., whereas the soft gum showed a retardation of only 28 to 33 deg. The difference in these two varieties has not yet been determined, the amount of mineral matter and the acidity being practically the same. It was found, however, that gum from tapped trees had a higher viscosity than that which exuded naturally ('4th Report Wellcome Research Laboratories, Khartoum'). A solution of gum arabic yields an opaque white gel with basic lead acetate—no doubt, due to the adsorption of PbH_2O_2. It becomes more glutinous on addition of borax and is not precipitated by tannic acid. It is insoluble in liquid phenol and in pyridine, in which gelatine is readily soluble.

On adding alcohol to a solution of the gum, it is precipitated, but more readily in presence of hydrochloric acid. The precipitate has been regarded as 'arabic acid,' but this cannot be the case, since the mineral matter adheres very strongly to the carbohydrates, and, unless the solution is dilute, the gum is precipitated almost unaltered.

Thus a solution precipitated once by alcohol in presence of dilute hydrochloric acid yielded a product containing 2·73 per cent. of mineral matter, while after three precipitations it still contained 2·24 per cent. In presence of sulphuric acid the precipitate contained 2·30 per cent. of mineral matter, while, in presence of ammonium oxalate, the precipitate contained 1·29 per cent. The proportion of galactan and araban did not appear to differ markedly from the original gum. After precipitating in this way, however, the gum does not dissolve to a clear sol, but is more or less turbid, and after about three precipitations with alcohol it ceases to be precipitated, but remains as a turbid sol, from which it deposits on addition of acids or electrolytes. On the other hand, Rideal and Youle ('Jour. Soc. Chem. Ind.' 1891, 60) found a difference in the optical rotation between the gum precipitated (amounting to about half the original) and that which remained in solution, from which they concluded that at least two substances were present. O'Sullivan obtained a similar result with 'pure arabin.'

Attempts have been made to utilise this reaction for estimating the gum in syrups (as also the amount of precipitate obtained with lead acetate in alcoholic solution), gum arabic yielding 85 per cent. of 'pure gum' calculated free from ash (A. C. Chauvin, 'Ann. Falsif.' 1912, **5**, 27–30, also X. Roques and G. Sellier, 'Ann. Chim. Analyt.' 1911, **16**, 218–220).

An interesting case of the mutual precipitation of two colloids is afforded by the interaction of gum arabic and gelatin, under certain conditions, which have been closely studied by F. W. Tiebackx ('Z. Chem. Ind. Kolloide,' 1911, **8**, 198–201, and 1911, **9**, 61–65). The precipitation takes place in acid solution only within certain limits depending upon the strength of the solutions. Thus, with 2 c.c. of a 0·5 per cent. gelatin solution and 2 c.c. of a 2 per cent. solution of gum, coagulation takes place with 2 c.c. of N/40 HCl, whereas with 2 c.c. of N/25 or N/125 acid, the solution, after becoming turbid, clears again. With a solution containing 0·5 per cent. of gelatin and 0·5 per cent. of gum arabic, a turbidity is produced when the acidity = ·002 N.HCl; on further addition of acid a precipitate occurs which passes again to a turbidity and at a concentration of 0·01 N the liquid becomes clear again. Increasing the percentage of gelatin and gum, or raising the temperature, restricts the action, until at a

concentration of 2 per cent. each of gelatin and gum, at a temperature of 80° C., there is no sign of flocculation. If, however, the proportion of gum is increased, a turbidity appears which again disappears on increasing the proportion of gelatin and gum. Strong solutions of gelatin and gum, *e.g.*, 50 c.c. of 50 per cent. solutions of each, yielded no precipitate with N/10 HCl, or stronger solutions of the acid. When sulphuric acid is added to a solution containing 0·5 per cent. of gelatin and 0·7 per cent. of gum, a turbidity occurs when the acidity of the solution is ±0·003N. A solution of 400 c.c. of a 0·4 per cent. solution of gelatin and 100 c.c. of a 2 per cent. solution of gum is coagulated by the addition of 500 c.c. of 6 per cent. acetic acid. The coagulum consists of an adsorption compound containing gelatin, gum, and acid, the gelatin being enclosed by the gum, which latter adsorbs the acid. On washing or drying at 100° C. the acid is removed. Two layers are formed, the lower one behaving in a similar way to globulin or casein in presence of electrolytes; the view being expressed that casein and other proteids may also be adsorption compounds, the constituents resembling one another both in properties and in composition. In the above reaction the acid may be replaced by salts, the most active being tartrates, citrates, phosphates, and acetates, followed by sulphates, chlorides, bromides, and iodides, the activity of the cations being in the following order, Na)K)NH_4)Mg)Zn). Salts cause the coagulum produced by acids to swell, the activity of the anions in this respect being in the order I)Br)Cl)SO_4)CO_3) and the cations K)Na) alkalies) alkaline earths). When, however, concentrated solutions of salts or those of $\frac{1}{8}$ gram molecule strength or less are employed, the already swollen transparent gel becomes again opaque. The tendency of a saline solution is to remove the acid, while in presence of salts greater concentration of acid is required to produce a given effect.

Gum arabic solutions show a very high osmotic pressure, which remains constant over a long period. Thus Pfeffer, using a copper ferrocyanide membrane, records a pressure of 7·2 c.m. of mercury with a 1 per cent. solution and 120·4 c.m. with an 18 per cent. solution (Ostwald, 'Solutions,' p. 94), while Moore and Roaf ('Biochem. Jour.' **2**, 39) and Edie ('4th Report Wellcome Research Laboratories, Khartoum'), using a parchment paper diaphragm, found for 6 per cent. solutions pressures of 114–170 m.m., and for a 10 per cent. solution 276 m.m. The reason for these high pressures, which remain almost constant after reaching a maximum, has not yet been explained; it may be due to the slow diffusion of the electrolytes associated with the carbohydrates, or it may be a swelling or imbibition pressure (pseudo-osmotic).

In testing gum arabic for commercial purposes the viscosity is the most important property (R. Hefelmann, 'Zeitschr. Offentl. Chem.' **7**, 195–198). C. Fromm ('Zeitschr. Annal. Chem.' 1901, **40**, 143-168) soaks strips of paper in solutions of the gums to be tested and notes the increase in weight and tensile strength of the paper which serves as a measure of the value of the gums for adhesive purposes. The latter author also states that on keeping gums a gradual change takes place in them which in the trade is known as 'ripening'; this change leads to a decrease in strength, viscosity, and acidity, at the same time there is an increase in the proportion of gelatinised insoluble gum.

The problem of the effect of colloids upon the precipitation of mineral matter is a very interesting one, which would well repay further study, not

only because of the remarkable results which have been obtained, but also in view of the difficulties which are encountered in many industries because of their presence. Generally speaking, colloids are more or less protective in their effect; that is to say, in the case of two solutions which in the ordinary way react to form an insoluble precipitate which settles easily, in presence of a colloid either no precipitate is formed or the precipitate is much more finely divided, and refuses to settle, or it settles much more slowly. Problems of this kind often occur in chemical works, sewage works, and in water filtration, &c., the remedies being either application of heat or addition of some chemical which in itself is colloidal, or which forms a colloidal precipitate of opposite sign, as, for instance, alum, ferrous sulphate, potassium permanganate, &c.; in the case of sewage also the colloidal matter may be destroyed or flocculated by bacterial action. On the other hand, it may be advantageous to form a highly flocculent precipitate instead of a crystalline one, as, for instance, in steam boilers, the deposit then being easier to deal with—a result which is brought about by the addition of colloids, *e.g.*, tannin and soda, infusion of straw, &c. The precipitation of mineral matter by slow diffusion of salts through colloidal jellies leads to the production either of spheroidal or nodular aggregates (Rainey, 'On the Mode of Formation of Shells of Animals, Bone, &c.,' published in 1858; also H. B. Stocks, 'Precipitation of Carbonate of Lime under Varying Conditions,' 'Jour. Soc. Chem. Ind.' 1912, **21**, 527) or to banded structure, which appears to explain the formation of mineral lodes (Hatschek, 'Jour. Soc. Chem. Ind.' 1911, 256; F. S. Shannon, 'Jour. Ind. and Eng. Chem.' 1912, 526–528, and E. Marriage, 'Z. Chem. Ind. Kolloide,' 1912, **11**, 1–5).

Other Soluble Gums.

There are two other types of soluble gums differing from gum arabic in their properties which are worth considering: the one the ghatti-gums, because of their high viscosity, the other the wattle-gums, because of their abundance.

Ghatti-gum is the product of *Anogeissus latifolia*, but the commercial varieties are mixed products containing the gums from several species, and therefore are very variable. The solutions of ghatti-gums are very much more viscous than those of gum arabic, and also contain more or less of a product which swells to a gel in water, but does not pass into the state of solution (metarabin). ('Colonial Reports,' No. 63, Imperial Institute, 'Report, Gums and Resins,' p. 160.)

The moisture in these gums ranges from 4 to 7 per cent., mineral matter 2 to 3 per cent., and potash neutralised on heating 0·22 to 3·99 per cent. (Rideal and Youle, 'Jour. Soc. Chem. Ind.' 1891, 160). Ghatti-gum contains more araban and less galactan than arabic gums.

The wattle-gums of Australia and South Africa are of two types—although there are many gradations—the one entirely soluble in water, the other leaving more or less swollen but insoluble gum. To the former group belong the gums of *Acacia farnesiana*, *A. ferruginea*, *A. leucophlœa*, &c., and to the latter gums from *A. decurrens*, *A. mollissima*, *A. vestita*, &c. For a full account of the wattle-gums see J. H. Maiden ('Pharm. Jour. **20**, 869–980). Several of the wattle-gums contain a low mineral content, *i.e.*, 1 per cent. or less, and they are all very low in viscosity. The wattle-gums are distinguished by containing a much greater proportion of galactan

and less araban than gum arabics. If the viscosity of these gums could be improved there would be a great demand for them; they are very plentiful, and exude freely in large tears or masses, often very fine.

A very large number of trees of other species and genera yield soluble gums, but none of these have ever come into extended use.

Tragacanth.

Tragacanth is employed in calico-printing, for painting on linen (A. H. Church, 'Chemistry of Paints and Paintings,' p. 70), in the preparation of lozenges, for cosmetic purposes, and in the manufacture of oil emulsions. This gum is the product of various species of *Astragalus* (Imperial Institute, 'Report on Gums and Resins,' p. 161), and it differs from gum arabic in that it is almost always the product of incisions. It shows distinct evidence of metamorphosed or swollen vegetable tissue, the cells containing a few granules which have the character of starch, which, however, appear to resist hot water to a considerable extent. The content of water varies according to the state of the atmosphere; normally this is about 17 per cent., but in moist air it may be as much as 26 per cent. (H. B. Stocks and H. G. White, 'Jour. Soc. Chem. Ind.' 1903, 4); it contains 3 to 5 per cent. of mineral matter, which is largely composed of carbonates (Rideal and Youle, 'Jour Soc. Chem. Ind.' 1891, 610), that produced by incision containing the larger quantity (Hilger and Dreyfus, 'Ber.' 1891, **33**, 610). The amount of acetic acid formed on heating with potash is much higher than gum arabic, corresponding to 15 to 26·61 per cent. of alkali neutralised (Rideal and Youle, Stocks), showing a different constitution. The carbon and hydrogen in this gum approximate to the formula $C_6H_{10}O_5$, but both galactan and araban are present, even more of the latter than in gum arabic; there is also a methylpentosan present, as fucose is found in the products of hydrolysis (A. Widtsoe and B. Tollens, 'Ber.' 1900, **133**, 132–143).

On heating tragacanth with water it swells very considerably, forming a stiff paste, even at 5 per cent. concentration, which by straining can be separated into a white translucent sol and an opaque insoluble gel, known as tragacanthine or bassorin. O'Sullivan ('Proc. Chem. Soc.' 1901, **17**, 156–157) states that the gum contains a series of gum acids similar to geddic acid, which he termed polyarabin-galactan geddic acids, and bassorin, which yields tragacanthan-xylan-bassoric acid by action of alkalies and xylan-bassoric acids on partial hydrolysis with acids. Xylan-bassoric acid is nearly insoluble in water, and bassoric acid insoluble, but the alkali salts are soluble.

According to Hilger and Dreyfus, on treating bassorin with 35 per cent. caustic potash and acidifying with acetic acid, oxybassorin $(C_{11}H_{20}O_{10})_2O$ is formed. If the alkaline solution is neutralised with acetic acid and precipitated by alcohol, the potassium derivative of oxybassorin is produced; this is soluble in water and yields insoluble calcium and silver derivatives by double decomposition. These salts do not respond to the usual tests for the metals, and therefore do not appear to be true salts. These are probably adsorption compounds of the bases. Tragacanth is not precipitated by ferric chloride, it is precipitated by alcohol and also by basic lead acetate. Dilute solutions of bassoric acid are precipitated by alcohol and also by electrolytes; it can be titrated, using

phenol-phthalein as indicator (T. von Fellenberg, 'Mitt. Lebensmittel, unters. Hyg.' 1914, **5**, 56–259).

Tragacanth gives with borax a slightly more viscous mass, a reaction which is sometimes made use of in detecting adulteration (W. L. Scoville, 'Drugg. Cir.' 1909, **53**, 116–117; also H. C. Fuller, 'Amer. Jour. Pharm.' 1912, **84**, 155–158). It can be distinguished by not containing oxydates.

Tragacanth yields a much more viscous solution than gum arabic, but does not form a continuous film on drying, breaking up into large curved flakes. The viscosity is lowered by heating under pressure. Tragacanth more nearly resembles starch than gum arabic in its properties. It shows only a slight osmotic pressure, *i.e.*, a 0·72 per cent. solution gave a pressure of 5 m.m. at 17° C. with a parchment paper membrane (Moore and Roaf, 'Biochem. Jour.' **2**, 39).

The commoner qualities of gum tragacanth, known in the market as 'gum trag' or 'hog gum,' is in larger and thicker pieces, white or yellow in colour, and often quite opaque. It yields a solution which is more pasty than real tragacanth and also contains more insoluble matter. The moisture in this gum is about 11 to 12 per cent., mineral matter 3·16, and potash neutralised after heating 8·14 per cent.

For certain purposes mixtures of two or more colloids are sometimes preferable to a single one (F. Beckmann, Ger. Pats. 219,651 and 223,709, 1908.)

In a general paper on thickenings for calico-printing from a colloid point of view, E. Austin-Müller ('Chem. Zeit.' 1910, **34**, 598–599) divides them into three classes:

(1) Homogeneous, *i.e.*, those which dissolve to a clear sol which can be filtered through paper—examples, gum arabic and better qualities of gum senegal.

(2) Heterogeneous. Those which form two phases, a sol and a gel, the latter retained by a filter, *e.g.*, tragacanth.

(3) Heterogeneous. Those forming micella-sols, which are entirely retained by a filter, *e.g.*, starch paste. The latter can be rendered more homogeneous by acetic acid. The products obtained from starch by roasting, *i.e.*, soluble starches and dextrins, fall between classes 2 and 3 or 1 and 2, according to their properties. By addition of NaHO they form homogeneous sols.

Insoluble Gums.

The gums which are insoluble in water exude naturally from cherry and peach trees, &c.; there are also certain gums found in India, known as Indian gum or Bombay gum, the products of species of *Sterculia*, and the gum of *Cochlospermum gossypium*, which have the remarkable property of spontaneously evolving acetic acid. H. H. Robinson ('Jour. Chem. Soc.' 1906, **89**, 1496) regards the latter as an acetyl derivative, and found that on distillation it yielded 14 per cent. of acetic acid.

Bombay gum and the gum of *Cochlospermum gossypium* are very similar in composition. They lose 19 to 21½ per cent. on heating at 100° C. (water and acetic acid), and contain 7 to 9 per cent. of mineral matter. On heating with alkali, the amount of KHO neutralised equals 13 to 16 per cent. They contain galactan and araban, but less of the former than in gum arabic; there is probably a third carbohydrate present.

On treatment with water they swell up very quickly to form nearly

transparent gels, which, however, are so brittle that they can be pulverised between the fingers into innumerable minute angular particles which do not coalesce.

These insoluble gums are not at present of any value, the chief interest in them commercially centring round the possibility of converting them into soluble products. Several patents have been taken out with the view of converting such gums into colloid sols, other colloidal products being also mentioned. Thus L. Kern (Eng. Pat. 21,370, 1891) purposes to render cherry, peach, and other gums soluble by heating with water under pressure; F. Fritsche (Eng. Pat. 1,353, 1908) prepares soluble gums by acting upon the products obtained from algæ and lichens—carrageen moss, agar, Iceland moss, &c.—East India gum, bassorine, &c., with sodium perborate after boiling with water under pressure; A. Boidin (Eng. Pat. 16,589, 1905) proposes to render starch, inulin, glycogen, gelose from agar-agar, gums and mucilages more readily soluble, by converting the phosphates which they contain into insoluble phosphates by addition of metallic salts or into monobasic acid salts by acidifying.

Vegetable Mucilages.

A variety of vegetable mucilages can be prepared by treating seeds, roots, &c., of various plants with water. These products, which were investigated many years ago by Fremy, Mulder, Chodnew, &c., were known as pectins or pectinous substances. Our knowledge of these materials needs revision. They are more nearly related to gum arabic than to the hemicelluloses. Pectose was the soluble colloidal material contained in beetroot; this was converted by means of an enzyme or ferment called pectase into pectin and subsequently into pectic acid, coagulation not occurring except in presence of CaO or a salt of Ca, Ba, or Sr. The coagulated mass is not pectic acid but a pectate of one of the alkaline earths (A. Mallevre, 'Bull. Soc. Chem.' 1895, **13**, 77–82). This looks like adsorption compounds.

The gelatinous material pectose is present in the pulp of ripe fruits, such as apples or pears, and in roots, *e.g.*, carrots and beetroot, in association with cellulose. It is insoluble in water (Fremy). By the action of the ferment pectase, or acids, alkalies, or milk of lime, pectose is converted into pectin or pectic acid; in other words, it is converted into a sol. Pectin is contained in the juice of ripe fruits, from which it is precipitated by alcohol in presence of HCl. It is soluble in water and is precipitated from the solution by basic lead acetate, also by $Ba(OH)_2$ and $Ca(OH)_2$ in excess, but not by NH_4HO, NaHO, HCl, H_3BO_3 or borax. On boiling an aqueous solution of pectin it becomes insoluble, being converted into parapectin (Fremy, Sidersky), parapectic acid ('Watts' Dict.,' vol. 4, p. 365), metapectic acid (J. Weisberg, 'Chem. Zeit.' **13**, 2). Parapectin is converted by dilute acids and bases into metapectin, and with concentrated solutions of the same into parapectic acid. Metapectic acid has an acid reaction; it is completely precipitated by lime and basic lead acetate. On prolonged heating it is converted into metapectic acid (J. Weisberg, 'Chem. Zeit.' **13**, 2). Pectous or pectosic acid is obtained by the action of pectase upon a solution of pectin, also produced by the action of cold solutions of the alkalies upon the same substances. It is a gelatinous substance, slightly soluble

in cold water, but quite soluble in dilute acids. On boiling with water it dissolves, but reverts to a gel on cooling. It is very quickly converted into pectic acid by boiling with water, by pectase, and by alkalies in excess. The pectosates form amorphous gels (Pelouze et Fremy). Pectic acid is formed by the action of alkalies upon pectin, also by the action of HCl upon beetroot pulp; it dissolves in boiling water, but reverts to a gel on cooling (Pelouze et Fremy). By long-continued boiling with water or by acids it is converted into parapectic acid; alkalies convert it into metapectic acid. Parapectic acid dissolves in cold water, and the solution on evaporation leaves a residue which resembles gum or gelatin. The solution reddens litmus and is precipitated on addition of a mineral acid, acetic acid, or $Ba(OH)_2$. It yields a gelatinous precipitate with alcohol. Metapectic acid is stated to be identical with arabic acid. It is soluble in water, forming turbid or heterogeneous sols, yields a barium salt and is precipitated by alcohol, but not completely by basic lead acetate in excess (J. Weisberg, 'Chem. Zeit.' **13**, 2).

We have therefore the following series of products:

Pectose	Metapectin	Parapectic acid
Pectin	Pectosic acid	Metapectic acid
Parapectin	Pectic acid	

The ultimate analyses of these products by various observers do not agree among themselves, therefore we do not know how many individual members really exist; one fact, however, is clear, that is, that they contain more oxygen and less hydrogen than the true carbohydrates and that they have for the most part acid functions which become more marked by partial hydrolysis, showing that they contain one or more COOH groupings. According to later nvestigations (E. Bourquelot, 'Comptes Rend.' **128**, 1241–1244, and Bourquelot and Herissy, 'Jour. Pharm. Chem.' 1899, **9**, 281–286), the pectens so far examined yield galactose and arabinose on hydrolysis, so that they probably contain galactan and araban. Cross and Bevan ('Cellulose,' p. 217) state that 'the pectic group of compounds may be regarded as compounds of carbohydrates of varied constitution with acid groups of undetermined constitution associated to form molecular complexes, more or less homogeneous, but entirely resolved by the continued action of simple hydrolytic agency.' According to S. B. Schryver and D. Haynes ('Biochem. Jour.' 1906, **10**, 539–547), 'pectinogen' is obtained by treating turnips with a solution of ammonium oxalate and precipitating with alcohol. It has acid functions, and when kept in alkaline solutions it readily reverts to pectin, which also has acid characters. It is soluble in alkalies and is precipitated as a gel on addition of acids. Analysis shows it to have the composition $C_{17}H_{24}O_{16}$. It yields furfural equivalent to one atom of carbon in each complex of C_{17}. Pectin would therefore appear to be an acid and not a carbohydrate.

Pectins are more particularly interesting since they form the basis of fruit-jellies, such fruits as currants, gooseberries, and apples being especially rich in these constituents. The mucilages of linseed, marshmallows, orchids, and other plants are also worth attention.

Several colloidal products from plants have been proposed for use from time to time, but very few have been found sufficiently valuable to

be retained in industry. A list of the more interesting patents in this connection is given below:

Preparation of a sizing material from the juice of linseed, hemp-seed, plantain-seed, &c. (F. C. Calvert, Eng. Pat. 164, 1857).

Obtaining fecula from bulbs of the lily type (R. I. C. Dubus, Eng. Pat. 2,801, 1857).

Preparation of a mucilage from quince-seeds (G. Norris, Eng. Pat. 2,240, 1861).

Preparation of a substance named 'parapectin' from the juice of the fruit of the arbutus tree by precipitating with alcohol. This substance resembles pectin but has greater consistency and strength (P. Mingaud, Eng. Pat. 1,649, 1865).

Obtaining a mucilaginous substance from flax, China grass, sorghum, *Phormium tenax*, and other fibre-yielding material by boiling with alkali (T. Gray, Eng. Pat. 1,058, 1866).

Preparing size from the fruit of the augustus palm (S. C. Dhondy, Eng. Pat. 7,458, 1891).

Preparation of a gum from plants of the Mesembryanthaceae family (R. Haddon (R. My Glyvares), Eng. Pat. 23,555, 1898).

Preparation of vegetable glue or sizing material from the palmetto palm and similar plants (F. Hepburn, Eng. Pat. 10,814, 1898).

Obtaining a glutinous substance from beetroot by treatment with SO_2 and neutralising with chalk. The acid calcium salt which is obtained is evaporated *in vacuo*. The product is rendered gelatinous by an alkali or ammonia, but this property is obviated by previous treatment with H_2O_2 (G. B. Ellis (F. Hornung), Eng. Pat. 22,788, 1898).

Using mucilage from linseed for sizing yarn (J. Pate, Eng. Pat. 2,645, 1901).

Obtaining 'viscine' from plants of the Ilex class (W. Loebell, Eng. Pat. 26,383, 1904).

Obtaining gum for sizing purposes from flax, hemp, and other textile fibres (H. Sefton Jones, Eng. Pat. 18,337, 1907).

Bacterial Gums.

The bacterial gums are of interest in connection with the mode of genesis of exudation gums and also as to their influence in certain industries such as sugar manufacture and brewing. A. Greig Smith appears to have been the first to connect the formation of gum, or gum flux, with bacterial action. In researches into the mode of formation of the gum from *Acacia perennis* (wattle-gum) he isolated from the twigs of the tree two kinds of bacteria, one of which, the most prevalent, named by him *Bacterium acaciæ*, when grown upon suitable media produced a slime of the araban-galactan class ('Proc. Linn. Soc. N.S.W.' 1902, Pt. III. Sept. 24). The view that a specific organism is responsible for the formation of gum is also held by Bean and Edie ('4th Report Wellcome Tropical Research Laboratories, Khartoum') as a result of their researches. Attempts to inoculate gum-bearing trees with this organism, however, led only to a decreased product of gum. Ruhland ('Ber. Deutsch. botan. Ges.,' 1906, XXIV. 393) holds the contrary opinion, although he was able to isolate a bacterium—*Bacillus spongiosus*—from diseased cherry-trees which formed a gum yielding only arabinose on hydrolysis. R. Greig Smith

('Centr. Bakt.' Par. II. 698–703) also discovered a bacterium—*Bacterium acaciæ*—in the gum of plum, cedar, peach, almond, and date trees. *B. persicæ*, found on peach and almond trees and *Cedrela Australis*, also probably influences the formation of gum. In a medium containing sucrose it forms a mucus or gummy matter which yields galactose and arabinose on hydrolysis. The gum of the fruit of *Sterculia diversiola* contains arabin and par-arabin (insoluble gum); these are stated to be produced by two organisms, *B. acaciæ* and *B. par-arabinium* respectively. Several varieties of the latter have been isolated and they produce par-arabin (*i.e.*, insoluble mucus) when grown under suitable conditions.

In the manufacture of sugar the juice sometimes becomes extremely viscous and very difficult to filter. This has been found to be due to an organism, *Bacillus levaniformis*, which forms a viscous or gummy product known as levan; this yields only lævulose on hydrolysis (Greig Smith and Thomas Steel, 'Jour. Soc. Chem. Ind.' 1902, 1381, 1904, 105). The product differs from that formed during the 'gummosis' disease or 'gumming' which takes place within the sugar-cane, the fibro-vascular bundles becoming filled with a viscous gum to which the name 'vasculin' has been applied by Cobb ('Agric. Gaz. N.S.W.' 1893, 777). Levan dissolves in cold water, but on dilution the sol becomes turbid and opaque, although no separation takes place either on standing or on centrifuging. It is not precipitated by basic lead acetate, but it forms an adsorption product with BaO containing 19·85 per cent. of the latter, similarly to starch.

Gum appears, however, to be present normally in unripe cane-juice, as this after evaporation thickens with acetic acid and on cooling sets to a solid mass. The amount of gum in the molasses was found to be 8 per cent. (Hazewinkel, 'Archiv Suikerind. Nederl. Ind.' 1910, **18**, 44–45).

Beet-juice sometimes becomes mucilaginous owing to a peculiar fermentation which is induced by an organism, *Leucostoccus mesenteroides*, resulting in the conversion of the sugar into a carbohydrate known as dextran or fermentation gum. Two varieties of this carbohydrate appear to be formed, one of which is soluble, the other insoluble in water. *Bacillus gummosis* also develops in sugar solution, forming a gum having the composition represented by the formula $C_6H_{10}O_5$ (Happ). It is remarkable that in both these cases at a certain period in the growth of the organism it swells up enormously, diffusing itself through the liquid, thus forming a mucilaginous fluid.

Ropiness also occurs in beer, milk, wine, infusions of Ipecacuanha, Radix Althæa, Senegæ, Folia Farfaræ, Folia Digitalis, &c., from time to time; in all cases the cause has been traced to the action of micro-organisms. (For further information on this subject see Lafar, 'Micro-organisms and Fermentation,' pp. 270–278.)

Hemicelluloses.

The hemicelluloses constitute a group of closely related substances contained in the seeds, roots, &c., of various plants, the cellular tissues of certain plants consisting largely of these products intimately associated with cellulose, to which they are also allied.

On heating with water, some of the hemicelluloses swell up enormously and pass into the state of colloidal sols, which are extremely viscous and which revert to non-rigid gels after keeping for a few days.

Hemicelluloses from seeds are employed in the manufacture of sizing materials (P. C. D. Castle, Eng. Pat. 10,822, 1905, C. V. Greenwood, Eng. Pat. 564, 1912). The hemicelluloses, no doubt, vary in composition, but that from the locust-bean (*Ceretonia siliqua*) consists of a complex of mannan and galactan in the proportion of about 2 : 1, mannose and galactose in these proportions being the products of hydrolysis (Bourquelot and Herissy, ' Compt. Rend.' 1889, **129**, 228, 231, also 1889, **129**, 391–393). Solutions of hemicelluloses of this type yield, on evaporation, clear transparent continuous films which have considerable tensile strength and are much tougher than films of nitrocellulose. In composition they approximate to the formula $C_6H_{10}O_5$ (H. B. Stocks and H. G. White, ' Jour. Soc. Chem. Ind.' 1903, 4, also C. F. Cross, ' Lectures on Cellulose, Inst. of Chem.' 1912). They contain but little mineral matter and are not acidic in character. Sols of the hemicelluloses show a very high viscosity, increasing enormously with the concentration, but heat has only a slight effect in decreasing it. Dilute acids lower the viscosity very considerably, especially the mineral acids ; alkalies increase the viscosity, especially of strong sols, which become glutinous or tenacious. Salts generally have very little effect except in strong solutions, in which case the complex is in many cases precipitated. Iron and copper salts, hydrogen peroxide, sodium peroxide, and potassium persulphate all lower the viscosity of the product. Heating under pressure and with organic acids renders the material quite fluid (C. V. Greenwood, Eng. Pat. 569, 1908), but partial reversion takes place after a time.

Hemicelluloses form adsorption compounds with bases such as $Ba(OH)_2$ and $Ca(OH)_2$ becoming more or less solidified and in diluted sol precipitated. Basic lead acetate forms a heavy solid white opaque gel, $KMnO_4$ and Fehling's solution also forms solid gels. Boric acid renders the gel more viscous, while the action is still more marked with borax, a solution of the complex being solidified to a brittle gel, while even in very dilute solution the material becomes so viscous that it ceases to flow and also does not wet the containing vessel. The mixing of viscous gels of this type with water is an interesting proposition ; the surface tension is so high that water will not penetrate. On stirring, the gel breaks up into small particles, which by long-continued stirring gradually absorb the water and coalesce, the mixture becoming homogeneous again. Friction is a considerable factor in the mixing, but, as dilution proceeds, the surface tension being progressively lowered, mixing becomes more and more easy. If the material is added to a large volume of water it is practically impossible to obtain a homogeneous solution. Mixtures of hemicelluloses with starch paste, some soluble starches, dextrin, if not too concentrated, Irish moss mucilage, and agar mucilage are easy to prepare, and homogeneous probably because the surface tensions are equal or nearly so ; but with hemicelluloses and gum arabic, gelatin, and strong solutions of dextrin the interfacial pressure must be considerable as there is no interpenetration, and although vigorously agitated they form granular or frothy heterogeneous mixtures which sooner or later separate into two layers of the different materials. The reason for this difference is not very apparent.

The hemicelluloses, consisting of mannan and galactan, react with tannic acid to form complexes, which in presence of excess of tannic acid appear as an opaque turbid sol with considerable reduction in

viscosity, immediately after mixing; upon standing, however, the viscosity progressively increases until after a few hours the product forms a soft gel which takes the form of the containing vessel; after a still further period the material separates into a stiffer gel and a clear supernatant liquid, about equal parts. On removing from the liquid, the gel progressively dehydrates until it forms a tough material like leather, and on fully drying it forms a hard solid. This product is an adsorption compound containing $C_{14}H_{10}O_9$ and $C_6H_{10}O_5$ molecules in the proportion 1 : 2. Owing to the special properties of this material, it is employed for the purpose of tanning, the colloidal carbohydrate having a restraining influence on the tannic acid, so that concentrated tanning liquors can be employed at the commencement and tanning completed in a few days (C. V. Greenwood, Eng. Pat. 5,018, 1910, and 7,635, 1915; also C. F. Cross, 'Lectures on Cellulose,' p. 38). On treating the material with water, tannic acid first dissolves, but on further dilution the complex becomes dispersed. Alcohol dissolves the whole of the tannic acid, precipitating the carbohydrate in the form of a flocculent gel. Some salts such as alum, Fe_2Cl_6, $FeSO_4$, and $ZnCl_2$, which yield precipitates with tannic acid, do not coagulate the hexosan-tannin complex, while others such as lead acetate, tartar emetic, $SnCl_2$, Na_2WO_4, and ammoniacal copper solution coagulate it.

The turbid complex becomes clear and much more viscous, *i.e.*, more dispersed at a temperature of about 42° C., reverting to the original condition on cooling; this change is strictly reversible. Alkalies and certain salts, *e.g.*, sodium benzoate and KCNS, also strong formaldehyde, sugar, glucose, and glycerine, cause a similar dispersion, the effect of hydroxyl, ions and groups, being most marked in this respect. Acids appear to have very little action.

The nuts of vegetable ivory (*Phytelephas macrocarpa*) and also probably of the dum dum palm ('Bull. Imp. Inst.' 1911, 105-109), coffee, date stones, &c., contain the carbohydrate mannan, which on hydrolysis with acid yields mannose. Vegetable ivory consists of almost pure mannan, which has been carefully studied by S. W. Johnson ('J. Amer. Soc.' 1896, 214–222). The nuts at present used in turnery work in place of real ivory are very large, extremely hard and tough white seeds. On treatment with water it is not dissolved, but it is readily soluble in 70 per cent. sulphuric acid, from which it is precipitated unchanged by addition of alcohol and ether. The mannan thus formed swells in water and partially dissolves; it is more readily soluble in alkalies. This would be a very useful product if a colloidal solution in water could be prepared.

There is also contained in woods generally a gummy product known as xylan, which yields xylose on hydrolysis. This dissolves in solutions of the alkalies, but is insoluble in water. It is contained in large quantity in the alkaline liquors of paper-pulp manufactories, but has not yet been utilised for technical purposes.

Seaweed Jellies.

Several algæ yield colloidal products when boiled with water, but only a few have been utilised for technical purposes. They differ in composition and properties from the colloids previously described, containing less carbon and more oxygen, and in addition 0·15 to 1·0 per cent. of nitrogen, but in what state of combination is not known. They contain galactan and

a methyl pentosan—fucosan—which hydrolyses to form the methyl pentose —fucose.

Irish moss grows extensively on the coasts of Ireland and Scotland, and was at one time largely used for sizing linen; it is still used to a limited extent. On soaking in water the plant breaks down to form a gelatinous mass, and on boiling with water it forms a colloidal sol which is quite fluid while hot, but sets to a gel on cooling. This material contains a considerable amount of finely divided cellular tissue and usually has a high mineral content, *i.e.*, about 18 per cent. (H. B. Stocks and H. G. White, 'Jour. Soc. Chem. Ind.' 1903, 4). Irish moss gel becomes less viscous with caustic soda; $Ba(OH)_2$ and Fe_2Cl_6 both yield precipitates and alcohol partly precipitates it.

Agar-agar is a Japanese product derived from a seaweed; it occurs in thin crinkled ribbons, and is extremely bulky. On heating with water it does not swell very appreciably or easily dissolve, but when solution is complete the liquid is very thin while hot, but on cooling it very quickly sets at about 50° C. to a solid brittle gel, which does not readily melt below the temperature of boiling water. These properties render it extremely useful for bacteriological investigations and other purposes. A solution containing only 1 per cent. of agar is quite solid at the ordinary temperature.

Agar contains about 20 per cent. of moisture and only about 1 per cent. of mineral matter. It has no acid characters. It is only slightly acted upon when heated with caustic soda solution. Alcohol yields a white curdy precipitate, and it is also precipitated by basic lead acetate, and tannic acid, which latter does not affect Irish moss jelly. It mixes readily with gum arabic and hemicellulose solutions.

Japanese isinglass is very similar to agar, sometimes being sold in the ribbon form and sometimes in rods about 1 in. square, which, however, consist merely of membranes filled with air bubbles, so that in this form it is equally bulky.

It contains about 23 per cent. of moisture and 2·9 per cent. of mineral matter, but likewise has a similar composition to agar (see also C. F. Cross, 'Lectures on Cellulose'). It dissolves more easily and more completely in water than does agar, and on cooling forms even a stiffer gel. The gel is clear at first, but after a time it becomes opaque. It yields a white cloudy precipitate with alcohol and is precipitated by basic lead acetate. It mixes readily with gum arabic solution.

Evaporated seaweed products in the form of scales are sold for sizing and finishing purposes under the names of 'Algin,' 'Blandola,' 'Norgine,' &c. Norgine is stated by E. Schmidt ('Chem. Zeit.' 1910, 1,149–1,150) to be the sodium salt of laminaria acid. It is probably an adsorption compound, as are several of the products mentioned in the patents below.

E. C. C. Stanford (Eng. Pat. 142, 1881, also 8,075, 1899; see also 'Journ. Soc. Chem. Ind.' 1886, 218) prepared a product (which he named 'algin') by heating marine algæ with caustic soda or sodium carbonate. The material was regarded by him as an acid, which he named 'alginic acid'; this combined with alkalies to form soluble compounds—algenoids—which could be used for a variety of purposes, notably for sizing. By adding metallic salts such as those of iron, mercury, silver, &c., to the alkaline solutions, precipitates were obtained which he regarded as insoluble alginates, proposed to be used for medicinal and other purposes. Most of these were soluble in ammonia. The British Algin Co., T. Ingham

and H. Bunzyl, took out patents for the preparation and application of such double alginates for waterproofing purposes (Eng. Pats. 25,187 and 25,537, 1905).

Preparation of a size for raw silk consisting of Japanese isinglass, gelatin, alum, spermaceti, and glycerine (J. F. Girard, Eng. Pat. 8,402, 1885).

Preparation of Irish moss for sizing paper (C. Morfitt, Eng. Pat. 8,148, 1886).

Preparation of mucilage or size (G. Laurean, Eng. Pat. 6,988, 1894), removing the saline ingredients preliminary to treatment with alkali; also S. Pitt (Laurean, Son & Co.), Eng. Pat. 28,356, 1898.

A solution of kelp is fixed with an alumina or other metallic salt for waterproofing purposes (Laurance & Co., Eng. Pat., 20,356, 1898).

Mixtures of starch and seaweed are used (M. Cerf, Fr. Pat. 317,942, 1902). A. Krefting (Eng. Pat. 7,913, 1903) precipitates the jelly as 'tangate' of lime and mixes the product with carbonate of soda. P. Jensen (Eng. Pat. 11,625, 1903) claims the use of agar, after treating with citric acid and filtration, for films for photographic purposes. W. F. Cooper (Eng. Pat. 2,156, 1907) also claims the use of agar for the same purpose. W. F. Cooper and W. H. Nuttall ('Phot. Jour.' 1908, **48**, 11–25) state that agar has certain advantages over gelatine for photographic purposes, it sets at a higher temperature, the viscosity is eight times greater; 1 per cent. solutions can be employed which enables thinner films to be obtained.

Preparation of mucilages (J. H. Laurean, Eng. Pat. 5,169, 1906, and F. F. Figgis, Eng. Pat. 22,247, 1906).

H. Bruhn and C. Timpke (Fr. Pat. 381,323, 1907) propose seaweed jelly as a size for use in paints.

Chem. Fabrik, Grüman, Landshoff und Meyer, A. G. and R. May (Ger. Pat. 240,832, 1911) claim the preparation of 'Norgine' insoluble in water and alkalies, formed by action of formaldehyde, also use of 'Norgine' as a protective colloid (Ger. Pat. 248,526, 1911). M. P. Gloess (Fr. Pat. 445,771, 1912) proposes to use sodium peroxide in preparing gums from seaweeds.

T. Ingham (Eng. Pat. 13,777, 1913) employs double alginates of alkali and heavy metal as sizing and dressing materials.

E. Hastaden ('Farber Zeitung,' 1909, **20**, 107–109) describes the use of carrageen moss in finishing.

Albuminous Substances.

The group of albuminous compounds have a similar percentage composition, containing a high percentage of nitrogen, but differ very considerably in their properties. They are all typical colloids, and several are exceedingly useful for technical purposes.

Albumin.

Albumin is not only valuable as a food product, but it is employed in calico-printing, leather-dressing, bookbinding, for clarifying liquids, &c. It is derived either from white of egg or from blood serum after purification with animal charcoal. Both forms are met with in commerce in the form of scales. Egg albumin is pale yellow and is used for fine purposes; blood albumin is red or brown and has an odour of meat. The latter can be distinguished also by containing an oxidase.

White of egg contains 10 to 12 per cent. of albumin, about 88 per cent. of water, rather less than 1 per cent. of mineral matter, and also about 1 per cent. of a carbohydrate. In dealing with white of egg, usually the hen's egg is implied. There are differences in the properties of the whites of eggs from different birds. For instance, the white of the duck egg has a bluish-cast and on heating coagulates to a stiffer gel.

Egg white consists of a glairy liquid portion and a glutinous portion; the latter, equal to about one-fifth of the whole, does not mix with the former but can be separated by means of a sieve. In what respect these two portions differ from one another we do not know, but there is certainly a difference in their alkalinity, the alkalinity of the glutinous portion being = to 0·473 per cent. of NaHO, and the more fluid portion, alkalinity = 0·585 per cent. NaHO. White of egg when fresh shows a distinct alkalinity to phenol-phthalein, showing the presence of HO ions, this being = to 0·026 to 0·159 per cent. NaHO; after keeping for a time, which may vary according to the quality of the egg, this reaction is not observed. The white is, however, always alkaline to methyl orange = to about 0·5 per cent. of NaHO. Addition of alkali to albumin results in a considerable increase in viscosity; with 20 c.c. white of egg and 3 c.c. N.NaHO the mixture sets to a solid gel after standing for a few hours; on further addition of alkali the albumin again becomes liquid, forming a thin fluid (alkali-albumin). Acids reduce the viscosity and finally coagulate the albumin, or, in solution, cause a flocculent precipitate. (For the effect of electrolytes on the viscosity, coagulation, and osmotic pressure of albumin see 'Colloids and their Viscosity,' Faraday Soc., March 12, 1913.) Acids, especially mineral acids, readily coagulate albumin; potassium ferrocyanide in acid solution is a powerful coagulant, being used as a test for traces of albumin. It is also coagulated by phenol, cresol, tannic acid, and by formaldehyde. It gradually yields a precipitate when shaken with ether or turpentine.

Egg white is purified for use in painting by adding dilute acetic acid till neutral and straining; this removes the glutinous portion and renders the material much more fluid. The painting can be rendered insoluble either by heat or by tannic acid (A. H. Church, 'Chemistry of Paints and Painting,' p. 63).

Dialysed albumin yields a clear gel with acetic acid; on heating, the mixture forms a clear fluid which gelatinises again on cooling. The viscosity of sols of albumin and acetic acid increases by keeping up to 18 to 20 days; the viscosity of albumen is also increased by addition of acetic acid up to 7·01 per cent.; further addition decreases the viscosity up to 11·22 per cent., when there is again a rise. Salts cause a rise in the rapidity of the reaction but not in the intensity (L. Zoja, 'Zeitschr. Chem. Ind. Kolloide,' 1908, **3**, 249, 269).

Albumin is readily salted out, salts of alkaline earths acting in this respect more powerfully than the alkalies, salts of zinc aluminium, and the heavy metals powerfully coagulate albumin.

Slaked lime and white of egg set to a solid; this mixture has been used as a cement for a very long time (D. C. Söuef (J. Schuberth), Eng. Pat. 1,225, 1862). A mixture of blood and slaked lime is a variant. White of egg in contact with iron or iron rust adsorbs $Fe_2(HO)_6$, becoming blood red in colour (iron albuminate), at the same time losing its viscosity.

Albumin in solution is coagulated at temperatures above 54°; at that

temperature it commences to coagulate and at 70° it is converted into a solid white gel. If, however, it is evaporated at temperatures below 40° it dries to form a pale yellow, transparent, brilliant film which is easily broken up into scales, in which form it is sold.

Salts, *e.g.* $(NH_4)_2SO_4$, lower the coagulation point of albumin. The effect is not so marked with egg albumin as with serum albumin, while milk albumin is much more sensitive (K. Micho, ' Zeitschr. Unters. Nahr. Genussm.' 1911, 646–654).

Dried albumin contains about 12 per cent. of moisture and 5 to 6 per cent. of mineral matter; the alkalinity equals about 2·4 per cent. of NaHO, but on boiling with water the alkalinity is increased to 4·13 per cent.; it would appear, therefore, that on coagulating a chemical change takes place. The alkalinity is probably due to phosphates.

Albumin forms homogeneous systems with gum arabic and with agar. The specific gravity of egg-white is 1·045. Harriette Chick and C. J. Martin (' Zeitschr. Chem. Ind. Kolloide,' 1913, **12**, 69–71) found that the densities of egg albumin, crystalline serum albumin, serum globulin, &c., compared with the densities of the same products in the solid state, show that on dissolution there is a contraction amounting to from 5 to 8 per cent. It was also found that with serum albumin and serum globulin the solution volume was independent of the concentration, but that with casein the contraction which takes place diminishes with increasing concentration.

Albumin adsorbs Ag_2O from a solution of the nitrate, forming silver albuminate; and it was found that in photography the whole of the silver was not removed from this compound after fixing with sodium thiosulphate (Luppo Cramer, ' Zeitschr. Chem. Ind. Kolloide,' 1907, **2**, 171–172). A compound of albumin and copper is also formed by adding $CuSO_4$ to a solution of albumen, with or without the addition of KHO. In the absence of alkali the product had an almost constant composition, the Cu and SO_4 being present in equivalent amounts, the product containing albumin 86·67, Cu 5·26, and SO_4 8·07. In presence of alkali the proportion of SO_4 in the compound decreased as the alkali was increased, until the product had the composition albumin 68·75, Cu 31·25 (G. Bonamartin and M. Lombardi, ' Zeitschr. Physiol. Chem.' 1908, **58**, 165–174).

When aqueous sols of albumin, tannic acid, and a metallic salt, &c., are mixed, a precipitate is obtained which contains albumin, tannic acid, and the metal. Using 20 per cent. sols in all cases the precipitates had the following molecular composition calculating tannic acid as a dibasic acid:

	Metal.	Albumin.	Tannin.
Ag salt . . .	18	32	50
Bi ,, . . .	14	40	46
Hg ,, . . .	15	50	35
Zn ,, . . .	10	48	42
Cu ,, . . .	9	50	41
Pb ,, . . .	16	45	39
Fe ,, . . .	5	60	35
Br ,, . . .	15	21	64
I ,, . . .	23	21	56

G. Grasser, ' Collegium,' 1911, 185–192 and 199–200.

A compound or combination of chloroform with an albumin has, according to C. S. Schleich (' Therapie der Gegenwart,' 1909, 138), been prepared. This preparation, which has been named ' desalgin,' contains 25 per cent. of chloroform in a solid colloidal form.

Both egg albumin and blood albumin are used for clarifying or 'fining' liquids. They owe their special functions to the fact that on heating, or by action of acids or tannin, the coagulum forms upon and around finely divided suspended matter; at the same time impurities may be adsorbed so that the liquids after settlement or filtration remain quite clear and bright.

Albumin or white of egg is used in baking for the preparation of light pastry, in which its film-producing properties are of great service.

Albumin is also very useful for glazing purposes and in the manufacture of leather finishes. (For the composition of leather finishes and the materials used in their manufacture see 'Leather Dressing,' by M. C. Lamb, pp. 263–282, also M. C. Lamb and A. Harvey, 'Jour. Soc. Dyers and Colourists,' 1917, 19.)

Egg-yolk, although it contains 33 per cent. of fatty matter, is also an albuminous product, seeing that it contains more albumin than egg-white, *e.g.*, about 15 per cent. It also contains about 1 per cent. of a carbohydrate and 1 per cent. of mineral matter. It is probably one of the most perfect emulsions known, since, however long it is kept, it shows no sign of separation or even on centrifuging or after considerable dilution. The albumin in egg-yolk, however, is not the same as that in the white, but consists, according to Gobley, of vitellin, nuclein, and cerebrin.

Egg-yolk is always slightly acid to phenol-phthalein, although alkaline to methyl orange, the alkalinity equalling about 0·87 per cent. of NaHO.

Egg-yolk is a very efficient emulsifying agent, being often used for this purpose. This property is, no doubt, due, partially at any rate, to the presence of lecithin in the fatty material; the amount of lecithin in the yolk equals about 10 per cent. Egg-yolk is employed in the preparation of 'fat liquors' for treating leather ('Leather Dressing,' by M. C. Lamb, pp. 214–228, also H. R. Procter, 'Leather Industries Laboratory Book,' 1908, p. 353), also in the manufacture of embrocations, being capable of emulsifying such incompatibles as acetic acid and olive oil or turpentine.

Certain salts, *e.g.*, NaCl, KCl, and KNO_3, cause a dispersion of the albumin in egg-yolk, the material becoming almost transparent. The same effect is produced with HCl, only that after a time the material sets to a gel and subsequently becomes opaque. 'Salted yolks,' that is, yolks containing about 10 per cent. of common salt, are an article of commerce.

Yolk of egg was one of the earliest mediums used in painting, being employed in ancient times as a medium for laying on the pigments in tempera painting. A. H. Church ('Chemistry of Paints and Painting,' 1892, p. 65) states that after a time the yolk becomes insoluble, the change being hastened by exposing the painting to sunlight, a practice which was quite common. Desiccated egg and yolk dried at a temperature of 100° F. also become gradually insoluble on keeping, this change being accelerated by heating at 100° F. or over, light not being necessary.

Casein.

Casein is the albuminoid of milk, which contains about 4 per cent., and in which it plays the part of an emulsifier, although in this respect it is not a perfect agent, seeing that milk separates on standing into two phases, the cream and skimmed milk. Cream separated by the centrifugal machine, however, is a perfect emulsion in which both the fat and casein

are more concentrated than in milk; in ordinary cream the two phases oil-casein and casein-water tend to progressive separation up to a limit. Milk also contains about 0 8 per cent. of a coagulable albumen which is stated to be identical with serum albumen.

Milk has an amphoteric reaction, *i.e.*, when fresh, it reacts feebly both acid and alkaline according to the indicator used; on keeping, it develops lactic acid by bacterial action, and at a certain acidity the whole solidifies to a gel, which after a time or with pressure separates into a solid 'curd' (casein or cheese) and a liquid 'whey.'

With hydrochloric acid the amount required to produce clotting was 20 c.c. of N/10 HCl for 20 c.c. of milk.

An investigation has been made into the influence of the hydrogen ion in milk clotting by C. Allemann ('Biochem. Zeitschr.' 1912, **45**, 346–358), who found that when different acids were added to milk together with rennet the time of clotting depended, not upon the acidity, but upon the hydrogen ion concentration. The clotting time diminishing up to a concentration of H ions of $1{\cdot}3 \times 10^{-5}$ the point at which acid alone caused coagulation. The effect of salts, *e.g.*, mixtures of phosphates and of sodium acetate and acetic acid, was also studied. It was found that the clotting points of whole milk, skimmed milk, and caseinogenate solutions showed certain differences.

When the precipitation of casein is brought about by acid in presence of a protective colloid, *e.g.*, gelatin or isinglass, the coagulum is much more diffuse, not separating in curds; hence these additions are useful for milk foods. The coagulum is also more finely divided when produced by kephir, koumiss, or youghout (*i.e.*, ferments producing lactic acid), the proteids being probably to some extent peptonised.

When albumin is added to milk and the mixture heated, the albumin and casein separate together as a complex in the form of a gel.

Commercial casein is prepared from skimmed milk by addition of rennet or acids (acetic, hydrochloric), in the case of rennet a certain amount of peptone may be formed by the digestive ferment. There is a difference in the behaviour of caseins according to the method of preparation. They contain about 11 per cent. of water and 7 per cent. of mineral matter, mostly calcium phosphate; usually also a small quantity of fat is present which has an influence on its properties.

On treatment with water, casein swells to a certain extent but does not dissolve; with NH_4HO there is a considerable increase in the swelling, but the mixture is heterogeneous; with caustic alkalies, alkaline carbonates, alkaline earths, and alkaline salts, *e.g.*, borax, sodium phosphate, &c., it forms various states of solution, those with alkalies showing the least viscosity. On heating with alkali there is a slight decomposition, ammonia being evolved and the liquid becoming extremely thin. Casein is also soluble in hydrochloric acid.

The amount of hydrochloric acid required for solution of 1 gram of casein at 1·25 per cent. concentration was found to be 32×10^{-5} equivalent gram mols of HCl, and the amount of caustic soda at 2 per cent. concentration $11{\cdot}4 \times 10^{-5}$ equivalent gram mols of NaHO (J. B. Robertson, 'Jour. Phys. Chem.' 1909, **13**, 469–489); casein is dissolved much less readily by solutions of alkaline earths (J. B. Robertson, 'Jour. Phys. Chem.' 1910, **14**, 377–392). On boiling casein with acids the rate of solution is directly in proportion to the strength and concentration of

the acid (*i.e.*, the H ion conc.). Acids are adsorbed by casein; thus from 100 c.c. of N/100 HCl nearly 50 per cent. was adsorbed in 3 hours; the amount varies almost directly with the concentration of the acid. With 1 gram of casein the equilibrium ratios at 0° C. with N/500 solutions were H_2SO_4 675, HCl 147, lactic acid 80, acetic 30. The affinity of casein for acids is, however, less than that for bases; 1 gram of casein combines with 9 c.c. of N/10 solutions of the hydroxides of Na,K,Li and NH_4 (F. Tangl, 'Pflüger's Archiv d. Physiol.' 1908, **121**, 534–549, 'Chem. Zeit.' 1908, 1, 1288).

Casein forms, with certain electrolytes, *e.g.*, KI, NaCNS, Na_2HPO_4, and KNO_3, fairly stable opalescent sols, which can be filtered; these are precipitated on addition of acids. It is insoluble in pyridine, but in a solution of pyridine it dissolves up to a maximum with increase of pyridine to $C_5H_5N.H_2O$. It is almost insoluble in formamide (S. Levites, 'Zeitschr. Chem. Ind. Kolloide,' 1910, 8, 4–8). Casein is rendered insoluble by formaldehyde. Tannic acid is absorbed by casein and can be quantitatively estimated, although the results are 1 to 1·5 per cent. too high (M. Nierenstein, 'Chem. Zeit.' 1911, **35**, 31).

Casein is utilised in many different ways in industry. It is employed along with lime, with or without pigments, as a washable distemper; as the lime carbonates it becomes insoluble. It is also used as a sizing material for textiles and paper (E. Sutermeister, 'Paper Making,' 1914, **33**, 140–143), being dissolved by ammonia (T. J. Denne and A. Hentschel, Eng. Pat. 2,429, 1872) or borax (H. V. Dunham, U.S. Pat. 897,885, 1908; see also F. W. Richardson, 'Jour. Soc. Dyers and Colourists,' 1909, 25, 4–3). Casein may be used as a cement along with sodium phosphate (W. A. Hall, Eng. Pat. 2,949, 1903), water glass (C. Wittkowsky, Eng. Pat. 9,070, 1905), slaked lime (C. W. Luther, Eng. Pat. 6,104, 1892), casein, rosin, and an alkali (C. and A. Bernstein, Ger. Pat. 270,200, 1913), sodium silicate and a strong solution of a salt of Ca, Ba, or Mg (A. Bernstein, Fr. Pat. 370,940, 1906).

Casein is a useful material for the manufacture of plastic masses, which can be readily moulded and set hard after a time. 'Galalith,' a combination of casein and formaldehyde, is a material of this kind which closely resembles bone or ivory and can be turned or carved (G. Bonitt, 'Zeitschr. angew. Chem.' 1914, **27**, 2).

Plastic masses can be formed by precipitating alkali-albuminate with acids and mixing the coagulum with a carbohydrate formed by the action of alkali solution on cellulose hydrate or starch. The mixture first liquefies and then progressively hardens (J. G. Jurgens and H. Timpke, Fr. Pat. 420,164, 1890). Combinations of casein and amines, amides or their derivatives (*e.g.*, aniline, acetanilide) are also employed (Soc. anon. L'Oyonnaxienne, Fr. Pat. 472,192, 1914). A substitute for horn or ivory is made from albumin or casein or alkali-albuminates by treating with the neutral esters of higher alcohols or amino-fatty acids which harden and coagulate them (W. Plinatus, Fr. Pat. 465,048, 1913). A mixture of casein and gelatin is treated with Na_2SiO_3 and then hardened with alum (F. von Kagenek, Ger. Pat. 281,541, 1913). Hydrochloric acid forms a gel with casein which is plastic (Eborit. Ges.m.b.H., Ger. Pat. 191,125, 1902). Casein is heated with water under pressure and the mass hardened with formaldehyde (Soc. anon. franç. de Chim. Ind., Fr. Pat. 425,204, 1910). A combination of casein, gum, glue, and rosin oil is also similarly

hardened with formaldehyde (Soc. anon. franç. de Chim. Ind., Fr. Pat. 425,204, 1910).

Casein is also used for waterproofing fabrics and for calico-printing, being rendered insoluble by vapours of formaldehyde (J. E. Bousfield (F. Cautin, G. Miglioretti, and G. Maffei), Eng. Pat. 1,160, 1901) or aluminium acetate.

Albuminous substances, particularly casein, are converted into sols by alkali sulphocarbonates, the same being coagulated by $(NH_4)_2SO_4$ and the product drawn into threads, films, &c. (Fr. Pat. 395,402, 1907, and addition of July 31, 1909).

For the preparation, properties, and applications of casein see also 'Casein and its Technical Utilisation,' by Robert Scherer, 1906 (Scott, Greenwood & Son).

Gluten.

Gluten is one of the proteids of flour, wheat-flour containing a coagulable albumin, gluten, and gliadin, the total being about 10 per cent. in the soft wheats and about 15 per cent. in the hard. When flour is first mixed with water it forms a very sticky tenacious mass, but after kneading for a little while it becomes quite plastic and may be freely handled. The baking properties of flour, *i.e.*, its capacity for imbibing water and retaining the gases generated during the fermentation, are very largely dependent upon the quantity and quality of the gluten present. Flour which has become deteriorated by storage or damaged by water has a weak gluten (*i.e.*, bacterial activity has lowered its viscosity); in such cases it forms very heavy and dark-coloured bread.

The baking properties of the flours from different cereals vary considerably; this is due not so much to the quantity of gluten present as to its quality, and also to the physical characters of the flour. Everyone is familiar, for instance, with the differences between wheat and oat bread.

Gluten is obtained from wheat-flour by washing it in a muslin bag in a stream of water, and kneading it till all the starch has passed through the cloth; this is the basis of the manufacture of macaroni and vermicelli and also of some of the American chewing gums. The gluten prepared in this way is crude, since it contains the cellular tissue of the flour. This method is employed in testing flour for sizing purposes. If the flour is fresh, the gluten is cream-coloured, stiff, and tenacious, but with deteriorated flour it is grey, soft, and pulpy, even sometimes passing along with the starch through the muslin. Gluten absorbs water to form a plastic mass, but after fully drying it does not again swell to the original extent. It is readily swollen by alkalies and by dilute acids, eventually passing into the state of a colloidal solution. The gluten of wheat-flour is rendered soluble by acetic and lactic acids formed during fermentation for sizing purposes, but it appears in other respects to be but slightly affected (H. B. Stocks and H. G. White, 'Jour. Soc. Chem. Ind.' 1903, 4). This is also the reason for the deterioration of baking-flour, and at one time it was corrected for by addition of alum, or copper sulphate, which rendered the gluten insoluble again and the bread whiter; the addition of these substances to flour is now illegal.

Fermented gluten dissolved in ammonia was proposed to be used in place of albumin for calico-printing, also for clarifying liquids and for photographic purposes (R. A. Brooman (C. Kestner), Eng. Pat. 2,428, 1864).

According to J. B. Wood ('Jour. Agric. Science,' 1907, **2**, 267–277), the properties of gluten are influenced by acids, by alkalies, and by salts. For instance, with HCl of N/100 strength it loses its coherence and commences to disintegrate, this effect increases with the concentration up to N/30, above which the opposite effect is noted, until with N/12 acid it becomes permanently coherent, less sticky, harder, and more elastic. Similar effects are noted with H_2SO_4, H_3PO_4 and $H_2C_2O_4$, but acetic, lactic, citric, and tartaric acids, irrespective of concentration, produce only loss of coherence with no subsequent recovery of strength. Soluble salts induce greater coherence with weak solutions of HCl, sodium sulphate acting more strongly than NaCl and Mg and Al sulphates still more so. Alkalies cause the gluten to become negatively charged, while acids have the opposite effect. Long-continued washing with water causes the dispersion of the gluten, owing to the CO_2 which it contains (J. B. Wood and W. B. Hardy, 'Proc. Roy. Soc.' 1909, **B. 81**, 38–43).

When moist gluten is placed in a solution of a salt, the salt is adsorbed by the gluten and at the same time water passes into the solution, the result being partial dehydration. The most active in this respect are the sulphates; chlorides and nitrates being apparently equal. Salts of the alkalies are more active than those of the alkaline earths. The 'partition constants' of $MgSO_4$ and $(NH_4)_2SO_4$, both of which are used as protein precipitants, are stated to be considerable (A. J. J. Vandervelde and L. Bosmans, 'Bull. Soc. Chim. Belg.' 1912, **26**, 249–254).

When gluten is bleached by SO_2 its elasticity is destroyed (M. G. Carteret, 'Bull. Soc. Chim.' 1909, 5, 270–272). SO_2 gas has been proposed as a solvent for gluten in the preparation of an adhesive (E. Donath, Ger. Pat. 172,610, 1905). Gluten is also brought into solution by means of a per- salt of an alkali (Erste Triester Reisschäl-Fabriks Aktien-Ges. Trieste, Eng. Pat. 8,203, 1910).

A patent has been granted to G. von Riegler (Fr. Pat. 461,131, 1913) for the preparation of artificial milk by dissolving gluten in KHO, salts, &c.

Soya beans (*Soya hispida*) contain about 38 per cent. of a proteid which resembles casein or gluten in its properties. In Japan and China it is the basis of several kinds of food, and it is also interesting, because it has been used more or less successfully in the manufacture of artificial milk, being converted into a colloidal solution by means of the phosphates of potash or soda and water and then emulsified with oil and lactose (F. Gässel, Fr. Pat. 451,447, 1912, Eng. Pat. 27,860, 1912, also J. Monahan and C. J. Pope, U.S. Pat. 1,104, 376, 1914); it has also been proposed as a plastic material, for the manufacture of artificial horn, bone, &c., for which purpose it is boiled with water and then coagulated with $Al_2(SO_4)_3$, or formaldehyde (R. Dodd and H. B. P. Humphries, Eng. Pat. 15,316, 1913).

Gelatin or Glutin.

Gelatin is the most typical of the reversible colloids, a solution containing it being very fluid when hot, but setting to a clear stiff gel on cooling, which again becomes fluid at a temperature of about 25°C. Dry gelatin imbibes a certain amount of water in the cold, the quantity depending upon, and is used a test for, the quality of the material, but it retains its shape and does not dissolve unless it is very impure. In the case of glue

which is moderately impure, a portion may diffuse from the swollen gel into the water.

Gelatin is used for food purposes, as an adhesive, in sizing paper and cloth, in the manufacture of photographic plates, printers' rollers and similar compositions, and as a size for painters' use.

In addition to having considerable viscosity, gelatin or glue solutions show in the most marked manner the properties of adhesiveness or 'stickiness,' which renders it so useful in many different trades. It also forms continuous films on drying, these being perfectly transparent when the material is pure, and having considerable toughness, except when the natural moisture is dried out, when it becomes brittle.

On long-continued heating, gelatin solutions lose viscosity; heating with acids and alkalies has a more pronounced effect, in some cases the product remaining fluid even at the ordinary temperature (basis of liquid glues); these products, however, have less viscosity and adhesiveness than the original material. Impurities, both organic and inorganic, tend to produce a similar effect, thus fish glue is often quite fluid and does not set to a gel, even when concentrated.

Moore and Roaf ('Biochem. Jour.' vol. 2, 39) found the osmotic pressure of a 10 per cent. gelatin, using a parchment paper membrane, to be 90 mm. at 40°, and 158 mm. at 91°. When injected into the blood, gelatin has the remarkable property of increasing its coagulability (H. Grau, 'Deutsche medizinische Wochenschrift,' 1910, 27, also Schultz, as quoted by Umber, 'Zeitschr. für arztliche Fortbildung,' 1912, No. 20). Gelatin swells in glacial acetic acid and on heating forms a fluid sol, used as a liquid glue; it is readily dissolved by crude carbolic and cresylic acids. It dissolves to the extent of 40 per cent. in a saturated solution of urea, the sol reverting to a gel on dialysing.

Gelatin is powerfully affected by even weak solutions of NaHO, KHO, and LiHO, which cause solution even in the cold; in presence of ammonia it swells considerably but does not pass beyond this stage. Alkaline carbonates and tribasic phosphates have the opposite effect, retarding solution, and with concentrated solutions entirely preventing solution even at 100° (A. L. Lumière and A. Seyewetz, 'Bull. Soc. Franç. Photo.' 1912, **3**, 159–163).

The effect of dilute acids, alkalies and salts upon gelatin has been closely studied by H. R. Procter ('Kolloidchem. Beihefte,' 1911, 2, 243–284), who found that the swelling of gelatin in highly ionised acids is considerably greater than in water, but weak acids, *e.g.*, H_3BO_3, CO_3 and SH_2, have not the same effect. Some of the acid is fixed either as a salt or by adsorption, the whole reacting to phenolphthalein but not to methyl orange. The swelling is partly due to the hydrogen-ion concentration. Swelling is retarded by salts, especially when concentrated. Alkalies also cause the swelling of gelatin, but in this case the swelling is not inhibited by neutral salts, and therefore appears to be due to the H-O ions and not to the cation. See also M. H. Fischer and A. Sykes ('Les Matières Grasses,' 1914, 4202–4204). The last-named authors state that with non-electrolytes the maximum dehydrating effect is observed only with high concentration, whereas, with electrolytes it is attained at a lower concentration, there being only slight increase in action for each successive increase in concentration.

According to J. L. de Bancels ('Compt. Rend.' 1908, **146**, 290–291), gelatin dissolves in water in presence of certain salts at the ordinary

temperature, the bivalent metals acting more strongly than univalent metals in equal concentrations.

The nitrates of the metals have a greater influence than the chlorides. The addition of electrolytes also causes the gelatin to dissolve in mixtures of non-electrolytes and water, *e.g.*, alcohol or acetone. On removing the salt by dialysis or by precipitation the gelatin separates.

The effect on gelatin of a large number of reagents, including acids, salts, phenols, &c., is described by A. L. Lumière and A. Seyewetz (' Bull. Soc. Chim.' 1908, 3, 743–750).

Certain salts, *e.g.*, those of Va, Ni, Co, and Cr, render gelatin insoluble (Lüppo-Cramer, ' Zeitschr. Chem. Ind. Kolloide,' 1909, 4, 21–23). Salts of Al and especially Fe_2Cl_6 have a similar effect (C. E. Millar, ' Jour. Soc. Chem. Ind.' 1900, 326).

With regard to the effect of chromium salts on gelatin, the action depends upon the constitution of the chromium compound employed. Thus when a small quantity of bichromate of potash is added to gelatin it has no sensible effect except after exposure to light, when the organic colloid becomes insoluble in hot water. The action of the bichromate is not well understood, although it is regarded as an oxidation process. The reaction, however, is made use of to a very large extent in photography, especially in the photomechanical processes. Dealing with gelatin from this point of view, C. W. Gamble (' Jour. Soc. Chem. Ind.' 1910, 65) states that it is a complex, the parent substance being ' collagen.' After heating for some time, gelatin passes into ' gelatose ' which does not gel, this change being also brought about by bacterial action and by proteolytic enzymes, especially trypsin. Bone gelatin and fish glue are classed as gelatoses. Gelatin and gelatose are precipitated by bromine in acid solution (A. H. Allen, ' Analyst,' 1897, 258) and also by chromic acid. Gelatin peptone is not precipitated by chromic acid, nor is it rendered insoluble after addition of bichromate and exposure to light; it also passes freely through a membrane. Gelatin peptone has a marked effect upon gelatin causing a greater tendency to dispersion. Glucose has a similar effect. Both these substances counteract the effect of bichromates after action of light, the film tending to dissolve on washing.

Gelatin has now almost entirely replaced albumin and collodion in the manufacture of photographic plates and papers. It is more reliable and more easily penetrated by the solutions employed; the introduction of this colloid for these purposes entirely revolutionised the photographic trade, and is largely responsible for the enormous developments which have taken place.

The preparation of photographic emulsions is based on the knowledge gained after years of practical work, and may be regarded as an industry founded upon the application of capillary phenomena.

There are many interesting points in connection with photography; for instance, Lüppo-Cramer (' Zeitschr. Chem. Ind. Kolloide,' 1907, 2, 171–172) found that silver oxide formed in a gelatin film by the action of NaHO caused the gelatin to become opalescent and insoluble in boiling water.

It is proposed to purify gelatin for photographic purposes by means of electro-osmosis, the fat and electrolytes passing through the membrane while the albuminoid substances are precipitated (Ges. für Elektro-Osmose, Eng. Pat. 21,448, and 21,484, 1914).

Electro-osmosis is likely to play an important part in industry in the

future, and several patents have been taken out in this connection for separating ions from colloids, for removal of water from peat, for removal of impurities from clay, &c.

Reverting again to the action of chromium compounds on gelatin, the effect of chromic compounds is also important since it has developed into an industry, that of 'chrome tannage.' According to Lumière and Seyewetz ('Bull. Soc. Chim.' 1903, 1077), 100 grams of gelatin fix from 3·2 to 3·5 grams Cr_2O_3 irrespective of the chromium salt employed. On the other hand, J. T. Wood ('Jour. Soc. Chem. Ind.' 1908, 384) found that the amount of chromic oxide taken up varied with the concentration of the salt; in dilute solution it amounted to 5 per cent. and in a strong solution 13·6 per cent., showing that it is an adsorption phenomenon.

Formaldehyde added to a gelatin sol raises the viscosity and finally solidifies it to an irreversible gel. This reaction is made use of in waterproofing, preparation of artificial silk, &c.

The maximum amount of formalin absorbed by gelatin is between 4·0 and 4·8 grams per 100 grams of dry gelatin (A. L. Lumière and A. Seyewetz, 'Bull. Soc. Chim.' 1906, 35, 872–879).

Compositions containing gelatin and glucose, invert sugar (treacle), or glycerine are employed in the manufacture of printers' rollers, 'jelly-graphs,' and for moulding purposes.

The permanent softening effect which these products have upon gelatin is probably due to their OH groups.

The gelatinising temperature or setting-point of gelatin is raised by partial purification by washing out some of the salts with water (K. Wenkiblech, 'Zeitschr. angew. Chem.' 1906, **19**, 1260–1262).

Alum and aluminium salts also raise the setting-point or 'harden' gelatin; in this respect the alkali aluminates have no action. In the case of alum or aluminium sulphate, the salt is first adsorbed, then by washing with water the SO_4 is removed, finally leaving Al_2O_3. The amount of Al_2O_3 adsorbed increases with increase in concentration up to a maximum of 3·6 per cent. Al_2O_3 (A. L. Lumière, 'Brit. Jour. Phot.' 1906, **53**, 573–4).

The most important reaction of gelatin especially in connection with tanning is that with tannic acid, the two being mutually precipitated in neutral or acid solutions, the gelatin then having a positive charge and the tannic acid a negative one. In a paper by J. T. Wood ('Jour. Soc. Chem. Ind.' 1908, 384) it is mentioned that Humphry Davy ('Proc. Roy. Soc.' Feb. 4, 1803) found the amount of precipitate to increase with the concentration, 100 parts of the coagulum containing 54 of gelatin and 46 of tannin. Lipovitz ('Jahres. Forts. Chemie,' 1861, p. 624) states that 100 parts of dry isinglass precipitates 65 of tannin. Rideal ('Glue and Glue Testing,' 1900, p. 111) found 42·7 gelatin and 57·3 tannin, Mulder (Allen, 'Com. Org. An.' iv. 463) says that 100 parts of dry gelatin precipitates 135 of gallotannic acid. R. Williams (Allen, p. 484), using 1 per cent. solutions of glue and tannic acid, and estimating the excess of tannic acid in the filtrate, arrived at the figures 77·5, 77·9, and 78·6 parts of tannin for 100 of gelatin. Böttinger, quoted by Procter ('Principles,' p. 63) found 66 per cent. of gelatin in the precipitate, which equals 50 parts of tannin to 100 parts of gelatin. These figures vary to such a degree as to prove that the reaction is not truly a chemical one. J. T. Wood (*ibid.*) found the amount of tannin precipitated by 1 part of gelatin to vary from 0·91

to 3·25 according to the concentration of the solutions and the time, and gives the following figures showing the composition of the precipitate :

	Unwashed.	Washed.
Gelatin . . .	25	32
Tannin . . .	75	68

According to Trunkel (' Biochem. Zeitschr.' 1910, **26**, 458–492), the reaction between tannin and gelatin is an adsorption phenomenon. Under certain conditions the whole of the gelatin and tannic acid can be precipitated quantitatively, the product then being insoluble and resistant to water. With excess of tannin the amount of tannin may be three times that of the gelatin, but the precipitate is then unstable and affected by water. By continued treatment with alcohol, 97 per cent. of the tannin can be removed, the remainder being retained. From the residue only about 6 per cent. of gelatin could be obtained in an unaltered condition. Trunkel also states that, with a freshly prepared solution of tannin, 1 part of gelatin required 0·7 part of tannin for complete precipitation, whereas with a solution 24 hours old only 0·4 part was required.

H. R. Procter (' Jour. Soc. Chem. Ind.' 1910, 329) also states that the precipitate is a colloidal combination, not a truly chemical (ionic) reaction, the precipitate is not definitely quantitative, and that the tannin can be removed to an almost unlimited extent by washing with water.

Gelatin in dilute solution, mixed with Japanese isinglass and also with agar, gives a somewhat similar reaction to that with gum arabic, a turbidity appearing which is increased on acidifying with HCl.

Chondrin from cartilage, although similar in its properties to gelatin, does not form such a stiff gel on cooling, it is also precipitated by alum and other salts which do not precipitate gelatin (Church, ' The Chemistry of Paints and Painting,' 1892, p. 65). Isinglass is somewhat similar to gelatin in its properties although it is not so easily soluble ; it is used in ' fining ' wine in which case it is coagulated, and carries down with it the finely divided suspended matter which rendered the liquid turbid.

The properties of gelatin are very considerably affected by impurities (decomposition products = gelatin peptone, &c.) and according to C. Dhéré and M. Gorgolewski (' Compt. Rend.' 1910, **150**, 934–936) the latter can be almost entirely removed by dialysis over a long period, *i.e.*, 1½ to 3 months, or by freezing a weak solution, when flocks of demineralised gelatin separate. Commercial gelatin carries a positive charge while demineralised gelatin is negative, therefore pure gelatin will be electrically neutral. Gelatin purified by these methods yields opalescent sols within certain limits of concentration. At 2 per cent. the sol is turbid, at 8 per cent. nearly clear, and at 10 per cent. quite so. Addition of alkali either partially or entirely removes the turbidity, but acids have not such a strong effect. A solution of such purified gelatin does not form such a strong gel as the original, a flocculent product settling out. Traces of electrolytes, *i.e.*, acids, alkalies, and salts, cause gelatinisation to take place ; this is the case with salts like KI which have an opposite effect upon ordinary gelatin.

According to J. T. Wood (' Collegium,' 1908, **12**, 494–5), the removal of the salts or the precipitation of lime by ammonium oxalate affects the tannin precipitate, rendering it less in amount. He is therefore of opinion that the predominant ions are those of calcium. Meunier states that a

small quantity of borax entirely inhibits the precipitation of gelatin by tannin, but boric acid does not influence it. Gelatin which has been precipitated by alcohol contains the whole of the mineral matter, and is, in fact, practically unaltered by the treatment.

In addition to the patents in connection with gelatin mentioned in the text the following are of interest :—

J. A. Swan (Eng. Pat. 3,303, 1866) claimed the use of chrome alum and other salts of chromium for rendering gelatin insoluble.

E. M. Knight and A. H. Hobson (Eng. Pat. 13,168, 1887) prepare a cement or gum by heating glue or gelatin with soda.

A. Zimmermann (Chem. Fabrik auf Actien vorm. E. Schering, Eng. Pat. 2,036, 1894) patented the application of formaldehyde for rendering gelatin and isinglass insoluble. The same firm claimed that the addition of a very small quantity of formaldehyde to glue materially increased its strength without rendering it insoluble (Eng. Pat. 4,696, 1894). J. Hofert (Eng. Pat. 4,697, 1894) uses gelatin as a waterproofing agent, rendering it insoluble with formaldehyde. An artificial silk (Vandaura silk) is manufactured from gelatin threads rendered insoluble by formaldehyde (A. Millar, Eng. Pat. 6,700, 1898 ; see also A. Millar, ' Jour. Soc. Chem. Ind.' 1899, 17, and C. E. Millar, *ibid.*, 1900, 326).

E. J. Mills (Eng. Pat. 8,847, 1895) proposed to use alkali and microbes, such as *Bacillus liquefaciens*, and liquid glue. Plastic substances are obtained by digesting ' ossein ' in NaHO solution (A. Heilbronner and E. A. Vallce, Eng. Pat. 20,548, 1906).

A mixture of gelatin, glycerine, formaldehyde (trioxymethylene), and an oxidising material, is employed for moulding purposes (B. Sauton, Eng. Pat. 27,616, 1906).

W. H. Perkin and Whipp Bros. & Tod (Eng. Pat. 23,030, 1907) claim the use of coal-tar creosote for dissolving gelatin.

The coagulation of colloids, *e.g.*, gelatin, glue, agar, casein, starch (commercial dextrin), is prevented by treatment with a salt of an organic sulphonic acid or derivative (The Arabol Man. Co., Fr. Pat. 394,173, 1908).

Use of lævulose for softening gelatin and glue (F. Evers, Eng. Pat. 25,145, 1909). See also A. H. Church, ' Chemistry of Paints and Painting,' p. 72.

COLLOIDS IN THE SETTING AND HARDENING OF CEMENTS.

By Dr. C. H. Desch, *Metallurgical Laboratory, University of Glasgow.*

The most important chemical investigation of the setting and hardening of calcareous cements is that which was submitted by Henry Le Chatelier in 1887 as a thesis for the Doctorate in the University of Paris. The setting of plaster of Paris was there shown to be due to the formation of an unstable solution of the hemihydrate in water, soon followed by the crystallisation of the less soluble dihydrate in spherulitic forms, the strength of the plaster after setting being due to the interlacing of crystals from neighbouring centres. Later investigations have only confirmed the truth of this explanation. In the case of Portland cement, it was shown that the basic silicates and aluminates of calcium contained in the cement clinker were hydrolysed by water, forming less basic salts and free calcium hydroxide. The most stable of these salts were determined

to be CaO, SiO_2, $2{\cdot}5H_2O$ and $4CaO$, Al_2O_3, $12H_2O$, and microscopical examination showed that all the products formed more or less spherulitic groups of crystals when the hydration took place in presence of an excess of water.[1] Le Chatelier's explanation was generally accepted. The alternative hypothesis, that 'the calcareous hydraulic cements owe their hardening mainly to the formation of colloidal calcium hydrosilicate,' was proposed by W. Michaëlis in 1893,[2] but attracted little attention until much later, when it was expanded into a detailed memoir,[3] at a time when the interest in colloidal substances had become much more general.

According to the hypothesis proposed by Michaëlis, the first effect of the action of water on the ground cement is the hydrolysis of aluminates. An unstable solution is rapidly formed, from which calcium sulphoaluminate, $3CaO$, Al_2O_3, $3CaSO_4$, xH_2O (due to the action of the calcium sulphate which is present in all commercial cements), and calcium aluminate separate as stable phases. The former compound is soluble, and crystallises readily in needles. The aluminate is less soluble, but is also crystalline under normal conditions, forming hexagonal plates. At this stage the silicates of the clinker are scarcely attacked. When the hydrolysis of the di- and tri-calcium silicates sets in, the only stable products are the hydrated metasilicate and calcium hydroxide, of which the latter crystallises in large plates, as observed by Le Chatelier. The case of the very insoluble metasilicate is different. The investigations of von Weimarn[4] have shown that a solid phase separating slowly from a moderately supersaturated solution forms well-defined crystals, that separation from a highly supersaturated solution favours the formation of crystal skeletons or spherulitic groups of needles, and that the formation of a highly insoluble product in a strongly supersaturated solution gives rise to the formation of gels. Michaëlis found that the hydrated calcium metasilicate almost invariably took the form of a gel, and that even the aluminate assumed that form if the solution were sufficiently supersaturated. The coating of the particles of ground clinker with a gelatinous sheath is readily observed under the microscope. The particles increase in size by the swelling of the gel—a fact which is very obvious in photographs taken at different intervals after the addition of water.[5]

This hypothesis has been challenged on the ground that if swelling actually took place, as in the absorption of water by starch grains or gelatin, the volume of the cement during setting must increase, and that no such increase does in fact occur.[6] This objection is based on a misunderstanding.[7] The individual particles increase in size, but

[1] *Thèse de Doctorat*, 1887, 'Recherches expérimentales sur la Constitution des Mortiers Hydrauliques,' Paris, 1904.

[2] *Chem. Zeit.*, 1893, **17**, 982.

[3] 'Der Erhärtungsprozess der kalkhaltigen hydraulischen Bindemittel,' Dresden, 1909. Partly in *Kolloid Zeitschr.* 1909, **5**, 9. An account of the hypothesis is given by C. H. Desch, *The Chemistry and Testing of Cement*, London, Arnold, 1911.

[4] The papers of P. P. von Weimarn in the *Kolloid Zeitschr.* for 1908-9 were collected in book form, *Zur Lehre von den Zuständen der Materie*, 2 vols., Dresden, 1914.

[5] H. Ambronn, *Tonind. Zeit.* 1909, **33**, 270.

[6] C. Schumann, *Tonind. Zeit.*, 1909, **33**, 465. See also A. Martens, *Mitt. k. Material-Prüf. Amt.*, 1897, **15**, 109.

[7] A. G. Larsson, *Tonind. Zeit.*, 1909, **33**, 785; W. Michaëlis, *ibid.*, 615. See also H. Kühl, *ibid.*, 556.

the total volume of cement and water diminishes during setting, a similar statement being true of the swelling of starch grains in water.[8]

A gelatinous coating having once been formed around the particles of clinker, which are thus protected from direct contact with the solution, a further series of changes sets in. Water is withdrawn from the gel by the unchanged core of clinker, which thus becomes progressively more hydrated, although even after many years the proportion of cement which has escaped hydration is always considerable. At the same time, according to Michaëlis, lime is adsorbed from the solution by the outer layers of the gel, which thus become harder and less permeable. On this view, the 'initial set' of cement corresponds with the hydration of the aluminates, forming crystalline masses comparable with plaster of Paris. The 'final set' is due to the formation of a silicate gel, traversed by crystals of calcium hydroxide, whilst the subsequent processes of desiccation and adsorption account for the progressive hardening of cement, which continues over a period of years.

A modification of this hypothesis was proposed by G. Becker,[9] according to whom the gelatinous membranes become stretched by the osmotic pressure, and then, through adsorption, undergo a change similar to that involved in the lignification of plant fibres. Becker also assigns a somewhat greater share in the process to the crystalline products of hydration.

Further evidence in favour of the colloidal hypothesis was adduced by Michaëlis. If the calcium compounds in Portland cement be replaced by barium, a similar series of changes takes place, but the product is not hydraulic, owing to the much greater solubility of the barium metasilicate, and the resulting compounds are entirely crystalline, so that the process of setting resembles that of plaster rather than of Portland cement. The presence of gelatinous material in briquettes of Portland cement after setting and hardening was observed by E. Stern,[10] opaque sections being examined by reflected light. Stern considered the gelatinous constituents to be alumina and calcium metasilicate, fine fibro-crystalline calcium aluminate also playing a part in the binding together of the mass, whilst the presence of calcium metasilicate in a crystalline form was doubtful.

The interest shown in the chemistry of hydraulic cements shortly after the appearance of Michaëlis's paper was such as to justify the publication of a special periodical devoted to the subject, which however only survived for eighteen months.[11]

An attempt was made to distinguish the various products of hydration by the application of organic dyes, which stain colloidal and zeolitic mineral substances selectively. By examining the behaviour of different substances, such as silica, alumina, calcium silicate, and calcium aluminate, when immersed in acid, neutral and alkaline solutions of such dyes as patent blue, anthrapurpurin, and methylene blue, and then testing hydrated cements with the same reagents, conclusions may be drawn as to the nature of the products contained in the cement.[12] The result

[8] H. Rodewald, *Zeitschr. physikal. Chem.*, 1897, **24**, 193.

[9] *Tonind. Zeit.*, 1909, **33**, 1493.

[10] *Ber.*, 1908, **41**, 1472; *Zeitschr. anorg. Chem.*, 1909, **63**, 160; *Mitt. k. Material-Prüf. Amt.*, 1910, **28**, 173.

[11] *Zentralblatt für Chemie und Analyse der Hydraulischen Zemente*, ed. F. R. v. Arlt, Halle a. S., 1910-11.

[12] S. Keisermann, *Kolloidchemische Beihefte*, 1910, **1**, 423.

of these observations is to show that calcium metasilicate is present both in the crystalline and the gelatinous forms, but that the tricalcium aluminate is entirely crystalline. The effect of stains varies considerably with the conditions of the experiment, and the present writer has been in many instances unable to confirm the observations of Keisermann. It should be added that so experienced an observer as Le Chatelier still considers that the process of setting of hydraulic cements is entirely one of crystallisation, and denies the influence of colloidal substances.[13] In repeating experiments on this point, it is important to remember that the process is not necessarily the same when a small quantity of cement is mixed with a relatively large proportion of water on a microscope slide and when, as in the practical use of cement or the making of test briquettes, the cement and water are mixed to a stiff paste ; and neglect of this fact, no doubt, accounts for some of the divergences between the conclusions of different investigators. The influence of the size of grain was pointed out by Wetzel in a criticism of the work of Keisermann.[14] An explanation of the hardening of cement in air, based on the assumption of the presence of colloids, which then absorb water vapour from the air, was given by L. Jesser.[15]

Experiments in which stains were used led F. Blumenthal [16] to the conclusion that crystalline monocalcium silicate was among the first products of hydration, together with the aluminate, and that the formation of the gelatinous silicate took place subsequently. The setting of the cement was then due to crystallisation alone, the later hardening being due to the binding together of the crystals by means of a gel, and the filling of the pores in the same manner.

The chemistry of Portland cement was set on an entirely new basis by the splendid investigations of the lime-silica-alumina system in the Geophysical Laboratory of the Carnegie Institution, Washington. As the result of these investigations, the constitution of cement clinker became known in detail, and it was then possible to consider the process of hydration as one of a definite series of chemical reactions. The study of the setting and hardening processes was taken up by the staff of the U.S. Bureau of Standards, whose results have been published in the form of monographs.[17] The general conclusions may be summarised as follows.

Tricalcium aluminate sets so rapidly that it is practically impossible to form it into test pieces, but it develops little strength. The hydrated product is mostly crystalline. The aluminate $5CaO,Al_3O_3$ also hydrates rapidly, forming an amorphous mass, which partly crystallises, the product being apparently the hydrate of tricalcium aluminate. Dicalcium silicate hydrates exceedingly slowly, and the product is entirely amorphous, except for the crystals of calcium hydroxide which make their appearance after a time. It is not believed that this amorphous or colloidal mass corresponds with any definite calcium silicate, but rather that it is an

[13] Private communication.
[14] *Zentr. hydraul. Zemente*, 1911, 2, 34.
[15] *Ibid.*, 51.
[16] Dissertation, Jena, 1912 ; *Silikat Zeitschr.*, 1914, 2, 43.
[17] A. A. Klein and A. J. Phillips, *U.S. Bureau of Standards, Technological Paper* 43 (1914) ; P. H. Bates and A. A. Klein, *Technol. Paper* 78 (1916). See also G. A. Rankin, *J. Franklin Inst.* 1916, 747.

indefinite colloid, which undergoes further hydrolysis in contact with an excess of water, progressively losing lime, until a residue of gelatinous silica remains. Dicalcium silicate is rendered more soluble by the presence of the soluble aluminate. Tricalcium silicate hydrolyses fairly rapidly, the product being of the same general character as in the last-mentioned case. A strong mass is obtained, and there is little doubt that pure tricalcium silicate would form a satisfactory Portland cement, as was in fact observed in the early experiments of Newberry.

According to the experiments of the Bureau of Standards, then, the initial set of Portland cement is due to the hydration of tricalcium aluminate, the product being amorphous. At the same time any sulpho-aluminate which may be present crystallises, and any excess of free lime becomes hydrated. Within twenty-four hours, the hydration of tricalcium silicate begins, usually becoming complete within seven days. Between seven and twenty-eight days, the hydration of the dicalcium silicate, which is present in considerable proportion in most cements, and the passage of the aluminate to the crystalline condition, are the chief stages in the process. Of these, the increase in strength is attributed to the formation of colloidal material, whilst the change from the colloidal to the crystalline state is regarded as involving an actual diminution of strength, the net effect being a gain. These results stand in conflict with many previous observations, but they have not yet been directly challenged.

Lastly, reference should be made to the influence of salts and other soluble substances on the rate of setting of cements. The addition of calcium sulphate to Portland cement for the purpose of retarding the setting has long been practised on the large scale, and the action of a number of 'catalysts,' both positive and negative, was studied by Rohland.[18] Michaëlis regarded the action as dependent on the change of solubility of the aluminates and silicates due to the presence of foreign salts, but Rohland, in more recent papers, has attributed it rather to their influence on the rate of coagulation of colloids.[19] The action of colloidal additions, such as tannin, straw infusion, &c., is very irregular, and no connection between the accelerating or retarding influence and the chemical composition has been found.[20] The changes in setting time which many cements undergo on storage, even out of contact with moisture, are probably of the same character, and the subject calls for much closer investigation than it has yet received.

NITRO-CELLULOSE EXPLOSIVES FROM THE STANDPOINT OF COLLOIDAL CHEMISTRY.

By E. R. Chrystall, *B.Sc.* (*Lond.*), *F.I.C.*

General Review.

The work which has been done on this subject from a scientific point of view is meagre in the extreme. The text-books on colloids barely mention the fact that nitro-cellulose forms colloidal solutions with organic solvents. The papers published for the most part deal with isolated cases investigated for the purpose of elucidating troubles in manufacture.

[18] P. Rohland, *Der Portland-Zement vom physikalisch-chemischen Standpunkte*, Leipzig, 1903.
[19] *Kolloid Zeitschr.* 1911, **8**, 251 ; **9**, 21.
[20] H. K. Benson, C. A. Newhall, and B. Tremper, *J. Ind. Eng. Chem.*, 1914, **6**, 795.

The reason for the neglect of this branch of work is undoubtedly due in large measure to the nature of the raw material cellulose. This substance, not occurring naturally in a pure state, has to undergo drastic treatment in the way of bleaching, cleaning, and so forth before it is suitable for the manufacture of nitro-cellulose, and all treatment of the cellulose has a large influence on the character of the finished product Furthermore the material largely employed in the explosive nitro-cellulose industry, namely cotton waste, is in itself waste product from the spinning mills. As most of the investigations are carried out by the chemists of the manufacturing firms, much of the work, probably the most valuable part, is never published.

The colloidal solutions which have been investigated fall roughly into two classes, those made with volatile solvents such as ether-alcohol, acetone, ethyl acetate, &c., and those made with comparatively non-volatile solvents, of which nitro-glycerin and camphor are the chief.

The principal work in the former class is that of Baker, who has investigated the viscosity of three important manufactured varieties of nitro-cellulose in various solvents, namely, acetone, ethyl formate, methyl, ethyl, propyl and amyl acetates, ethyl butyrate, aceto-ethyl-toluidide, ethyl tolyl ethyl carbamate, ethyl phthalate, ether-alcohol, ether-methyl alcohol, &c. He finds that the viscosity follows the law $N=N_0(1+AC)^R$, where N and N_0 are the viscosities of solution and solvent respectively, C is the concentration, and A and R are constants depending both on solvent and solute.

In general the viscosities of nitro-cellulose solutions are diminished by all treatment which the substance or its raw material undergoes, such as bleaching and cleaning the cellulose, stabilising the nitro-cellulose by boiling, heating the nitrating mixture or the finished product, and heating or exposing to light the solutions under investigation. The presence of traces of impurities in all stages of the work also adversely affects the viscosity. These causes, as well as fundamental differences in the cellulose itself, account for the varying and discordant results obtained by different workers.

In the system nitro-cellulose-nitro-glycerin, *i.e.*, blasting gelatine, the problem is to obtain a stiff gelatinous colloid which will not exude nitro-glycerin and will transmit the explosive wave with certainty. The preparation of a suitable nitro-cellulose, which in practice forms about 7–8 per cent. of the mixture, is a matter of great delicacy both in selection of raw material and method of procedure, and practically no information is available on the subject.

Hargreaves explains the behaviour of blasting gelatine by assuming a webbed structure of nitro-glycerin and nitro-cellulose, through the meshes of which free nitro-glycerin passes. As the colloid ages, more and more of the free liquid is absorbed into the gel, thus producing the state of insensitiveness to detonation which is one of the great troubles of the manufacturer. Comey (' Seventh Int. Cong. App. Ch.') has, however, shown that liquid nitro-glycerin when confined in narrow tubes is but a poor transmitter of the detonating wave. Experiments by G. W. MacDonald and the writer have shown that the problem is still more complicated, and that, although the colloidal condition of the system has a large influence on the detonation of the explosive, its behaviour can be totally altered in a few hours merely by exhausting the air which

is mechanically entangled in it during the process of incorporation. Aubert and Nauckoff have patented the addition of cork dust for the purpose of retaining air in the explosive. Colloids can be made with nitro-cellulose and liquid aromatic nitro-hydrocarbons. These are used both with and without nitro-glycerin. When used with the latter the purpose is to prevent the freezing of the explosive, since on thawing dangerous exudation of nitro-glycerin is apt to occur by the liquid not being completely re-absorbed into the colloid. Modern propellant explosives all consist of a colloided nitro-cellulose with or without admixture of nitro-glycerin. Investigations into their micro-structure and other properties have been carried out, but have not been published.

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CELLULOID FROM THE STANDPOINT OF COLLOIDAL CHEMISTRY.

By E. R. Chrystall, *B.Sc.* (*Lond.*), *F.I.C.*

1. Celluloid: Viscosity and its importance for the Chemistry of Celluloid in theory and practice. H. Schwarz, 'Zeitschr. Chem. Ind. Koll.' 1913 (12), 32–42.
2. Celluloid: The Absorption of Gases, by V. Lefebure, 'J. Chem. Soc.' 1914 (105), 328–337.
3. Celluloid Chemistry: Problems of, and the necessity of colloid chemical views in this industry. H. Schwarz, 'Kolloidchem. Beihefte,' 1914 (6), 90–126.

General Review.

The literature on the celluloid branch of the nitro-cellulose industry, as far as colloidal chemistry is concerned, is as meagre as that on the explosive branch. Three papers have been found bearing on this subject:

(1) The author deals with the viscosity of alcohol celluloid solutions

in connection with ageing, percentage of camphor, temperature, and brittleness of the finished product.

(2) The absorption, diffusion, and equilibrium curves of carbon-di-oxide are determined and discussed.

(3) The stability of the colloid against latent acidity is considered, together with the so-called antacid treatment. The efficiency of the latter the author considers to be dependent on the size of the molecular aggregates suspended in the colloid.

COLLOIDAL AND CAPILLARY PHENOMENA IN THEIR BEARINGS ON PHYSIOLOGY AND BIO-CHEMISTRY.

By Prof. W. RAMSDEN, *Bio-Chemical Laboratory, University of Liverpool.*

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